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STUDY OF (1:1) COMPLEX OF  
POTASSIUM 3-METHYL-3-PENTOXIDE:3-METHYL-3-PENTANOL  
IN TRIGLYME AS A BASE/SOLVENT SYSTEM FOR  
E2 ELIMINATION REACTIONS

by

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## INTRODUCTION

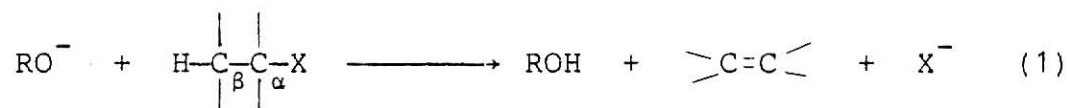
Elimination reactions of acyclic and alicyclic derivatives to produce olefins are a major class of organic reactions which have been the subject of considerable research for the last four decades. The most extensively studied set of elimination processes have involved the reactions of various bases with alkyl halides or certain derivatives of alcohols; the alcohol derivative must yield a stable anion for the elimination to be useful. Other related base-induced elimination reactions yield the multiple bonds of alkynes, carbonyl groups, and imines. The unsaturated products are useful not only as end products, but also as intermediates in organic synthesis. In order to optimize the yield and to control the stereochemistry in the elimination product, an understanding of the reaction mechanism is essential. In an elimination reaction, two bonds must be broken and one or more new bonds (including that of the multiple bond) must be formed. These multiple changes afford a variety of mechanistic possibilities ranging from multistep sequences involving charged intermediates to concerted processes. Many of the fundamental mechanistic problems of organic chemistry are encountered in elimination reactions.

Alkene-forming  $\beta$ -eliminations have attracted the most attention. It can be safely concluded from the published studies that the yield of olefin from a particular substrate depends on the reaction conditions which influence both the

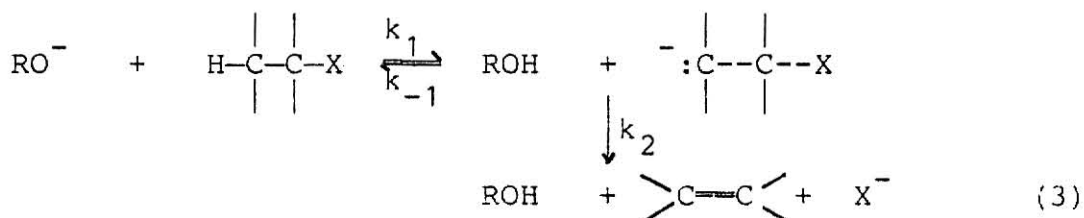
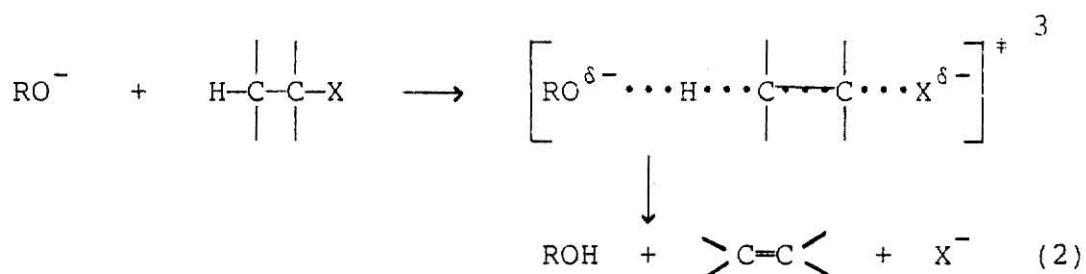
mechanism and the relative importance of substitution and elimination for a particular mechanism. Several base/solvent systems have been studied and various mechanisms have been proposed. However, there is no unified picture. N. S. Issacs<sup>1</sup> points out, "The subject of polar elimination reactions has, in recent years, become blurred and fraught with controversy". Of the several bases investigated so far, the alkali metal alkoxides have proven to be of greatest interest in studies of elimination reactions.

#### A. Mechanisms of Olefin Formation by Alkoxide-Promoted $\beta$ -Elimination Reactions.

During the past decade, the mechanisms for base-promoted  $\beta$ -elimination reactions have been reviewed by several groups<sup>2-4</sup>. Mechanistic possibilities for olefin formation by alkoxide-promoted  $\beta$ -eliminations (eq. 1) include the E2 and the E1cB elimination reaction mechanisms. In the E2 mechanism (eq. 2) both the  $C_\beta$ -H and  $C_\alpha$ -X bonds cleave concertedly via a



single transition state. In the E1cB mechanism, the two steps involve rupture of the  $C_\beta$ -H bond followed by scission of the  $C_\alpha$ -X bond (eq. 3). Substrate properties



which lead to elimination by the E1cB mechanism include a  $\beta$ -hydrogen that is acidified by a strongly activating sulfonyl or cyano group and/or a very poor anionic leaving group<sup>2,5</sup>. The substrates used in the present study do not possess these latter properties. Therefore, the E2 mechanism is considered to apply to these reactions.

#### B. The Variable E2 Transition State.

The E2 mechanism involves concerted, but not necessarily synchronous, making and breaking of the four affected bonds in the transition state. Different timing of bond making and bond breaking may give rise to transition states with carbanionic character at  $\text{C}_\beta$ , carbonium character at  $\text{C}_\alpha$ , and varying degrees of double bond character. It is important to note that the character of E2 transition states is dependent on the base and solvent, as well as on the substrate structure<sup>3-5</sup>.

### C. Alkoxide Base/Solvent System.

It is now well established that alkali metal alkoxide ion-pairing interactions are important even in polar solvents, such as ethanol and dimethyl sulfoxide. For example, Brandstrom<sup>6</sup> reports that 1.0 M EtONa in EtOH contains only about 20% of dissociated ethoxide ions. Therefore, the presence of various base species in a given base/solvent system must be considered. The dominant associated alkoxide-alkali metal ion species which are present in aprotic solvents of low polarity have been investigated by a variety of physical techniques<sup>7</sup>. These studies show that tert-BuOK exists primarily as a tetramer in toluene, benzene, diethyl ether, 1,2-dimethoxyethane, tetrahydrofuran, and pyridine. Tert-BuONa ranges from a tetramer in diethyl ether, tetrahydrofuran, and pyridine, to approximately an octamer in benzene, carbon tetrachloride, and cyclohexane. X-ray and mass spectrometric data substantiate these results<sup>8-10</sup>.

The 3-methyl-3-pentoxide:3-methyl-3-pentanol (1:1) complex in triglyme as the solvent was used by McDonald and Curi<sup>11</sup> as the base/solvent system for the elimination of exo-2-bicyclo-[2.2.0]hexyl tosylate to give the corresponding olefin. The reaction was carried out for 5 min at 25°C, and the olefinic product isolated by trap-to-trap distillation. This base/solvent system was shown to have a number of advantages over several other base/solvent systems investigated. However, the generality of this procedure was not established<sup>11</sup>.

## OBJECTIVE OF THIS INVESTIGATION.

The objective of this investigation was to explore the broader synthetic utility of potassium 3-methyl-3-pentoxide:3-methyl-3-pentanol (1:1) complex (3M3P-OK:3M3P-OH) in triglyme as the base/solvent system for E2 elimination reactions.



## EXPERIMENTAL RESULTS

The alkyl tosylates were synthesized from the corresponding alcohols by the usual pyridine method.<sup>23</sup> The alkyl bromides were obtained from a commercial source.

All of the  $\beta$ -elimination reactions were carried out in triethylene glycol dimethyl ether (triglyme) with the crystalline 1:1 complex potassium 3-methyl-3-pentoxide:3-methyl-3-pentanol (3M3P-OK:3M3P-OH) as the base at 25°C for two hours under a dry nitrogen atmosphere. The reaction product was removed from the mixture by distillation and the olefin content was determined from the <sup>1</sup>H-NMR spectrum of the distillate by integrating the area of the olefinic protons using benzene as the internal standard. The amount of unreacted tosylate ester was determined from the distillation residue using a Varian 5000 HPLC (10  $\mu$ L loop injector) with a UV detector set at 260 nm. The HPLC peak areas were measured and compared to those of a working-plot of detector response (area) vs. ROTs concentration. Yields are reported on the basis of the mmoles of reactant employed and the mmoles of olefin formed. A by-product from certain reactions was formation of the corresponding ether presumably formed by an S<sub>N</sub>2 displacement mechanism. Efforts to isolate these ethers failed mainly because their boiling points were similar to that of triglyme, the reaction solvent. The results are summarized in the Table I.

Table I. Summary of Product Data for Reactions of Alkyl Tosylates and Bromides with Potassium-3-Methyl-3-Pentoxide: 3-Methyl-3-Pentanol in Triglyme at 25°C.

Rxn.	Alkyl Group	Leaving Group	Olefin Product(%) <sup>a</sup>
1	<u>exo</u> -2-norbornyl	OTs	77 ± 5
2	<u>exo</u> -2-norbornyl	Br	72 ± 3
3	<u>endo</u> -2-norbornyl	OTs	10 ± 3
4	cyclopentyl	OTs	60 ± 2
5	cyclopentyl	Br	64 ± 1
6	cyclohexyl	OTs	80 ± 2 <sup>b</sup>
7	cyclohexyl	Br	83 ± 1 <sup>b</sup>
8	1-pentyl	OTs	68 ± 3
9	1-pentyl	Br	61 ± 2
10	2-pentyl	OTs	57 ± 2 <sup>c</sup>
11	2-pentyl	Br	54 ± 2 <sup>c</sup>
12	3-pentyl	OTs	54 ± 3
13	3-pentyl	Br	53 ± 1
14	1-hexyl	OTs	66 ± 1
15	1-hexyl	Br	62 ± 2

<sup>a</sup>Yields were based on RX employed.

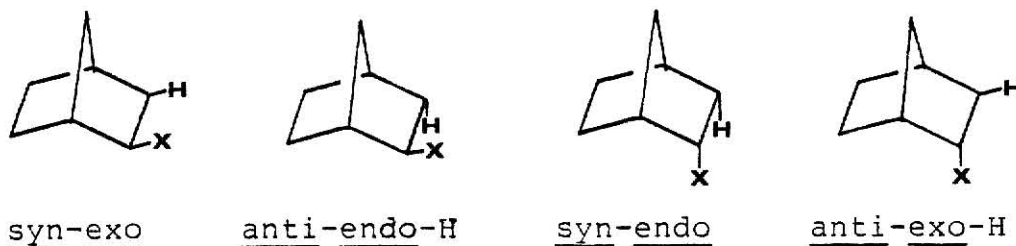
<sup>b</sup>Yields were determined by <sup>1</sup>H-NMR of an aliquot from the reaction mixture after 2 hrs. To isolated yields were 20% from ROTs and 23% from RBr.

<sup>c</sup>The olefin product contained 76% 1-olefin and 24% trans-2-olefin from ROTs, and 75% 1-olefin and 25% trans-2-olefin from RBr.

## DISCUSSION OF EXPERIMENTAL RESULTS

(a) 2-Norbornyl Derivatives. 2-Bicyclo[2.2.1]heptyl (norbornyl) derivatives have been extensively used as substrates for mechanistic studies of bimolecular elimination reactions. Reacting conformations for elimination reactions are limited because of the rigidity of the bicyclic carbon skeleton.  $\beta$ -Elimination can occur in only one direction and the product norbornene is highly strained ( $E_s = 20.7$  Kcal/mole)<sup>12</sup>. Two complications often arise in studies of E2 reactions in the norbornyl system; (i) competitive occurrence of 2,6-elimination giving nortricyclene, and (ii) the marked tendency for an E1 mechanism to occur in ionizing media.

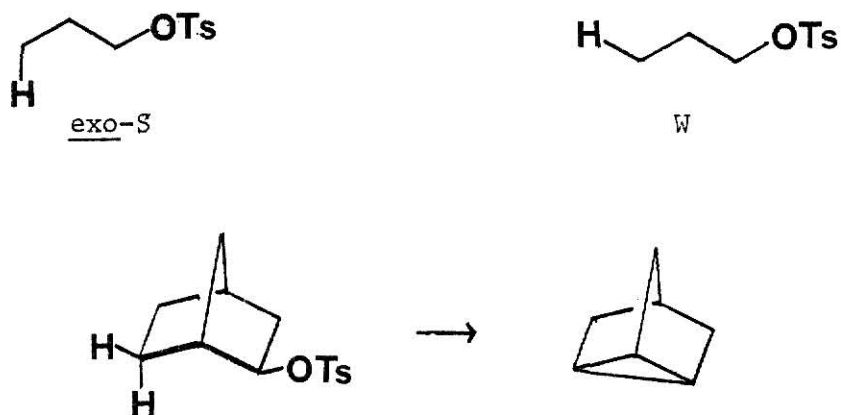
In  $\beta$ -eliminations from 2-substituted norbornanes, four stereochemical pathways are possible, syn-exo, anti-endo-H, syn-endo, and anti-exo-H. Brown and Liu<sup>14</sup> have shown that in the  $\beta$ -elimination reactions of the exo- and endo-2-norbornyl



tosylates, the exo-C<sub>3</sub>-H is the proton preferentially transferred to the base. It has also been shown that exo-2-norbornyl tosylate,<sup>14</sup> bromide,<sup>15</sup> and chloride<sup>16</sup> undergo primarily syn-exo bimolecular  $\beta$ -elimination, rather than anti-endo-H elimination. From endo-2-norbornyl chloride, the anti-exo-H pathway

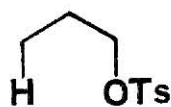
is strongly favored (84%) over that of the syn-endo pathway (16%) under E2 reaction conditions.<sup>16</sup>

Kwart, et al., obtained norbornene (98% yield) containing no nortricyclene when exo-2-norbornyl bromide was heated with potassium 3-methyl-3-pentoxide in 3-methyl-3-pentanol at 130°C.<sup>14</sup> The norbornene produced was considered to have been formed by an E2 mechanism. Dehydrotosylation of exo-2-norbornyl-endo-3-d<sub>1</sub> tosylate under the same conditions was complicated apparently due to an E1 component. However, when the reaction was carried out with potassium 3-methyl-3-pentoxide in p-cymene (containing some 3-methyl-3-pentanol), the products were norbornene and nortricyclene in a 19:1 ratio assumed to be formed by a "pure E2" elimination reaction. It was proposed that only when the ionization of the C<sub>2</sub>-OTs bond had been properly suppressed by use of a sufficiently low dielectric medium could the E2 reaction pattern be observed.<sup>14</sup> The findings of Nickon and Werstik from the reaction of exo-2-norbornyl tosylate with tert-BuOK/tert-BuOH revealed that at high base concentration loss of a proton via the exo-S geometry was preferred over that of the W-geometry in formation of nortricyclene.<sup>17</sup>

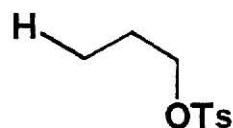


In the present experiments using the 1:1 complex of 3M3P-OK:3M3P-OH in triglyme at 26°, norbornene was exclusively obtained from exo-2-norbornyl tosylate in 76% yield. There was no evidence for the presence of nortricyclene (GLPC analysis showed no peak corresponding to the retention time of authentic nortricyclene<sup>18</sup>). From exo-2-norbornyl bromide, a 70% yield of norbornene (no nortricyclene) was obtained under identical reaction conditions. Since the yields of norbornene from the tosylate and bromide are comparable, and since the reactions were carried out under the same reaction conditions, the transition states in these two reactions should be similar.

Elimination reactions from endo-2norbornyl brosylates have been reported under several conditions.<sup>18</sup> Studies with endo-2norbornyl-exo, exo-2,3-d<sub>2</sub>chloride have revealed the operation of anti-exo-H mechanism in these elemination reactions.<sup>15,16</sup> A study by Nickon and Werstiuk showed that the formation of nortricyclene prefers the U geometry over the endo-S geometry from endo-2-norbornyl tosylates.<sup>16</sup>



U

endo-S

When endo-2-norbornyl tosylate was allowed to react with the 3M3P-OK:3M3P-OH (1:1) complex in triglyme at 25°, norbornene was exclusively produced, although only 10% of the

starting tosylate was consumed. The fact that no nortri-cyclene was obtained suggests that the steric bulk of the base in this medium makes it incapable of abstracting the endo-C<sub>6</sub>-H.

(b) Cyclopentyl and Cyclohexyl Derivatives. In the present work, cyclopentyl and cyclohexyl tosylates and bromides were allowed to react with the 3M3P-OK:3M3P-OH (1:1) complex in triglyme at 25°C. The results are summarized in Table I, reactions 4-7. The results show that the cyclohexyl derivatives yielded more olefinic product than did the cyclopentyl ones. No unreacted tosylate was recovered when either of the substrates was employed. In case of cyclohexyl tosylate and bromide the <sup>1</sup>H-NMR of the aliquot taken from the reaction mixture after 2 hrs of reaction time indicated the presence of cyclohexene in 80% and 83% respectively. However, only 20% of the olefin could be distilled from the reaction mixture using the tosylate and 23% from the bromide. A model study showed that cyclohexene could be quantitatively distilled from a mixture of this olefin and triglyme containing some 3M3P-OH.

(c) Acyclic Alkyl Derivatives. The data from Table I, reactions 8,9,14, and 15, showed that the yield of olefin produced from the 1-pentyl and 1-hexyl derivatives was comparable for a particular leaving group. As expected for these closely related substrates, the amount of olefin formed is independent of the R group in the alkyl chain.<sup>19</sup> E2

$\beta$ -elimination reactions from unsymmetrical 2-alkyl derivatives are complicated and have received a lot of attention. Hughes and Ingold showed that the direction of bimolecular elimination appears to follow two conflicting rules, the Saytzeff and the Hofmann rules.<sup>20</sup> It is now well known that the ratio of 1-olefin/2-olefin depends on the alkyl substrate, the leaving group, and the base-solvent system used.<sup>21</sup> In the present studies, 2-pentyl tosylate and bromide were found to give similar yields of total olefinic product containing 75% 1-olefin and 25% trans-2-olefin. As expected, the symmetrical 3-pentyl tosylate and bromide gave 54% and 53% yields, respectively, of 2-olefin.

## SUMMARY

The  $\beta$ -elimination reactions of various alkyl tosylate esters and bromides were studied to determine the synthetic potential of potassium 3-methyl-3-pentoxide:3-methyl-3-pentanol (1:1) complex in triglyme at 25°C as the base/solvent system. The reactions were carried out under identical conditions. The exo-2-norbornyl derivatives gave a 75 $\pm$ 5% yield of norbornene without any detectable amount of nortricyclene. The endo-2-norbornyl derivative afforded only 10 $\pm$ 3% of the olefin. The 1-pentyl and 1-hexyl derivatives gave comparable yield (65 $\pm$ 2%) of the 1-olefins. The 2-pentyl derivatives produced 55 $\pm$ 2% yield of a mixture of olefins containing 1-pentene (75%) and trans-2-pentene (25%). The 3-pentyl derivatives formed 2-pentene in 54 $\pm$ 3% yield. The cyclohexyl derivatives afforded more olefin (81 $\pm$ 2%) than did the cyclopentyl derivatives (62 $\pm$ 2%).

Thus, the 1:1 complex of potassium 3-methyl-3-pentoxide:3-methyl-3-pentanol in triglyme appears to be a useful base/solvent system for  $\beta$ -elimination processes. The important advantage of this system is that the reactions can be carried out at room temperature under non-ionizing conditions.



EXPERIMENTAL SECTION<sup>22</sup>

Preparation of Potassium-3-methyl-3-pentoxide:3-Methyl-3-Pentanol (1:1) Complex. To 300 g of freshly distilled 3-methyl-3-pentanol (3M3P-OH) from  $\text{CaH}_2$  in a 1 L three-necked, round bottomed flask equipped with a dry nitrogen inlet and outlet system, a magnetic stirrer, a thermometer, and a condenser, was added 19.5 g of freshly cut potassium metal and stirred at room temperature for 1 hr. The reaction mixture was heated to about  $65^\circ\text{C}$  to melt the unreacted potassium which, prior to melting, appeared to be coated with a layer of insoluble alkoxide that prevented further reaction of the metal. The melted potassium was emulsified by vigorous stirring until all of it reacted (approximately 2 hrs.). The excess 3M3P-OH was removed by distillation with a 12" Vigreux column at  $65^\circ\text{C}/100$  torr until a syrupy residue remained. While this residue was hot, the pressure was slowly reduced to 0.2 torr (the receiving flask containing 3M3P-OH was cooled in dry ice). This pressure was maintained for about 3 hrs. at room temperature, after which the solid residue was dissolved in 300 mL of ether. The ether solution was transferred to a 2 L round bottomed flask, the ether removed (rotary evaporation; nitrogen was used to bring the system to atmospheric pressure), and the residue mixed with 1000 mL of pentane. The resulting mixture was vigorously shaken and cooled in an ice-water bath for 2 hrs. producing long, thin needle-shaped crystals. The crystals were filtered

under nitrogen, washed once with 100 mL of pentane and dried under vacuum (0.2 torr) at room temperature for 6 hrs, to afford 25 g of the white, solid product. A second crystallization from the mother liquor (after removing some of the solvent) gave 20 g more of the product. Titration of a known amount of this product with a standard solution of HCl and using phenolphthalein indicator, gave 0.5 equivalent of base-component, which indicated a 1:1 ratio of 3M3P-OK/3M3P-OH. This 1:1 complex was soluble in ether, diglyme and triglyme, Curiously, this complex was not very soluble in 3M3P-OH and DMSO.

Preparation of Alkyl Tosylates. The alkyl tosylates used in this study were prepared from their alcohols and tosyl chloride by the usual pyridine method<sup>23</sup>. A solution of 3-5 g of the alcohol in 50-75 mL of pyridine (distilled from and stored over KOH pellets) in a 125 mL glass-stoppered Erlenmeyer flask was cooled to 0°C and treated with 1 molar excess of freshly recrystallized tosyl chloride (recrystallized from chloroform-petroleum ether, mp 68°C). After solution was complete the flask was placed in a refrigerator for 24 hrs. The reaction was followed by the development of yellow or pink color, followed by the separation of pyridine hydrochloride as long needles. When no more precipitate appeared to be forming, the entire mixture was poured with stirring into 300-400 mL of cold water. This mixture was extracted with three 125 mL-portions of ether (pre-cooled to 0°C), and the combined extracts were washed with 150 mL of 6N H<sub>2</sub>SO<sub>4</sub>

(pre-cooled to  $0^{\circ}$ ) followed with two 50 mL portions of 10% NaCl solution. This ether solution was placed in 500 mL, three-necked, round-bottomed flask equipped with a condenser, a thermometer, a bleed-tube connected to an ammonia tank, and cooled in an ice-water bath.  $\text{NH}_3$  was passed through the magnetically stirred solution at the rate of 200 mL/min. for 2.5 hr. The white precipitate of *p*-toluenesulfanamide produced, if any, was removed by filtration. The ether solution was rapidly washed with two 75 mL portions of 10% NaCl solution pre-cooled to  $0^{\circ}$ , dried over  $\text{MgSO}_4$ , and the solvent removed by rotary evaporation. At this stage either a solid or an oil was obtained.

For purification, the tosylate (oil or solid) was dissolved in the minimum quantity of petroleum ether at room temperature. After stirring with Norit, the mixture was filtered. The clear, colorless solution was cooled slowly to  $-75^{\circ}$  in a dry ice-acetone bath with scratching to induce crystallization. If crystallization occurred, the crystalline alkyl tosylate was filtered and dried in vacuo (0.2 torr) at room temperature. If no precipitate was obtained after cooling, the solvent was removed by rotary evaporation, to afford an oily mass. The oil was further dried in vacuo (0.2 torr) at room temperature and used directly.

The physical properties and  $^1\text{H}$ -NMR spectra of the alkyl tosylates prepared by this procedure are listed:

exo-2-norbornyl tosylate (m.p.  $57-58^{\circ}$ , Lit.<sup>14</sup>  $61-62^{\circ}$ )

$\delta_{\text{TMS}}^{\text{CCl}_4}$  0.8-1.7 (m, 8H), 2.1-2.5 (m, 2H), 2.4 (s, 3H), 4.5

(broadened t, 1H), 7.2-7.6 (q, 4H);

endo-2-norbornyl tosylate (oil)  $\delta_{\text{TMS}}^{\text{CCl}_4}$  0.8-1.7 (m, 8H), 2.2-2.4 (m, 2H), 2.4 (s, 3H), 4.8 (broadened m, 1H), 7.2-7.6 (q, 4H);

cyclopentyl tosylate (oil)  $\delta_{\text{TMS}}^{\text{CCl}_4}$  1.5-2 (m, 8H), 2.4 (s, 3H), 4.9 (broadened m, 1H), 7.2-7.6 (q, 4H);

cyclohexyl tosylate (m.p.  $46^\circ$ , Lit.<sup>24</sup>  $46^\circ$ )  $\delta_{\text{TMS}}^{\text{CCl}_4}$  1.5-2.1 (m, 10H), 2.4 (s, 3H), 4.9 (broadened m, 1H), 7.2-7.6 (q, 4H);

1-pentyl tosylate (oil)  $\delta_{\text{TMS}}^{\text{CCl}_4}$  0.6-1.8 (broadened m, 9H), 2.4 (s, 3H), 3.8 (t, 2H), 7.2-7.6 (q, 4H);

2-pentyl tosylate (oil)  $\delta_{\text{TMS}}^{\text{CCl}_4}$  0.6-1.8 (broadened m, 10H), 2.4 (s, 3H), 4.5 (sextet, 1H), 7.2-7.6 (q, 4H);

3-pentyl tosylate (m.p.  $41^\circ$ , Lit.<sup>25</sup>  $41-43^\circ$ )  $\delta_{\text{TMS}}^{\text{CCl}_4}$  0.6-1.8 (broadened m, 10H), 2.4 (s, 3H), 4.5 (quintet, 1H), 7.2-7.6 (q, 4H) and

1-hexyl tosylate (oil)  $\delta_{\text{TMS}}^{\text{CCl}_4}$  0.6-1.8 (broadened m, 11H), 2.4 (s, 3H), 3.8 (t, 3H), 7.2-7.6 (q, 4H).

Availability of Alkyl Bromides. The alkyl bromides used in our studies were purchased from Aldrich Chemical Company. The bromides were distilled and dried over molecular sieves before use.  $^1\text{H-NMR}$  showed that they were 98-99% pure.

Purification of Solvent (Triglyme). This solvent was obtained from Eastman Company. It was refluxed and distilled under vacuum from calcium hydride just prior to use.

General Procedure for the Elimination Reactions of Alkyl Tosylates and Bromides using Potassium 3-Methyl-3-pentoxide: 3-Methyl-3-pentanol (1:1) in Triglyme. To 6.05 g (25 mmole) of the 1:1 complex dissolved in 25 mL of triglyme in a 50 mL three-necked, round-bottomed flask (equipped with a dry N<sub>2</sub> inlet and outlet system, a magnetic stirrer, and a water-bath at room temperature) was added 5 mmole of the alkyl tosylate or bromide in one portion. The reaction flask was stoppered to maintain a small positive nitrogen pressure, and the mixture was stirred at room temperature for two hrs. It was observed that after the tosylate was added a white, bulky precipitate began forming. After the two hr. reaction time, a known volume of sample of the mixture was withdrawn and checked for the olefin content by <sup>1</sup>H-NMR. The reaction products were trap-to-trap distilled. The volatile materials collected in the traps were dissolved either in CDCl<sub>3</sub> or CCl<sub>4</sub> and the olefin content was measured by <sup>1</sup>H-NMR. Within the experimental errors, the two quantitations agreed well, except for the cyclohexyl derivatives. A small amount of triglyme and 3M3P-OH was present as revealed by NMR.

The reaction mixture left behind after distilling off the olefin was run through a column of alumina. The column was washed using 50 mL of dry ether. Ether was carefully removed by rotary evaporation and the remaining solution was checked for unreacted tosylate using a Varian 5000 HPLC (10 µL loop injector) with a UV detector set at 260 nm using a solvent program that employed 40% CH<sub>3</sub>CN/H<sub>2</sub>O as eluant for 4

minutes, and then increased the gradient to 100% CH<sub>3</sub>CN after 10 minutes. Authentic samples of known concentration (approximately 0.5 mg/mL) were run on the HPLC under the same conditions at the same time. Areas were measured and the amount of unreacted tosylate was calculated. No appreciable amount of unreacted tosylate was detected except in case of exo- and endo-2-norbornyl tosylates. No attempt was made to check for the unreacted bromide.

Procedure for the Elimination Reactions of 3-Pentyl Tosylate and Bromide using Potassium 3-Methyl-3-pentoxide:3-Methyl-3-pentanol (1:1) in Triglyme. The reactions were carried out in the manner described in the general procedure. The percentages of 1-pentene and 2-pentene were determined by GLPC analysis using 10% silicon oil (UC-W 98, 6 ft x 0.125 in.) column at 50°C. The volatile components of the product mixture were carefully trap-to-trap distilled. The 1- and 2-pentene mixture obtained was diluted with helium and a known volume was injected into the gas chromatograph. The percentages of the two olefins were calculated by comparing their peak areas with the standard plot constructed from known percentages of 1- and 2-pentene (diluted with helium) vs. the detector response.

Preparation of a Mixture of Norbornene and Nortricyclene from endo-2-Norbornyl Tosylate. To 35 mL of freshly distilled nitrobenzene in a 50 mL three-necked, round-bottomed flask,

equipped with a dry nitrogen inlet and outlet system, a thermometer, and a trap-to-trap distillation arrangement, was added 2.66 g (10 mmole) of endo-2-norbornyl tosylate in one portion. The mixture was heated to about 110° for 3 hrs. The product mixture was distilled (10 torr) from the reaction mixture and was collected in a receiver cooled in a dry ice-acetone bath. GLPC analysis of the product mixture using 10% diisodecyl phthalate on Chromosorb W (8 ft x 0.25 in.) column at 50° (injection port 130°, detector 120°) indicated the presence of norbornene and nortricyclene in the ratio 1:3, which was identical to that reported.

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22. (a) Melting points were determined on a Kofler hot stage. (b) <sup>1</sup>H-NMR spectra were obtained on Varian T-60. (c) HPLC analyses were carried out using a Varian model 5000 liquid chromatograph with a Varian MCH-10, universal, reverse-phase column. (d) GLPC analyses were done on Hewlett-Packard 5750.
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STUDY OF (1:1) COMPLEX OF  
POTASSIUM 3-METHYL-3-PENTOXIDE:3-METHYL-3-PENTANOL  
IN TRIGLYME AS A BASE/SOLVENT SYSTEM FOR  
E2 ELIMINATION REACTIONS

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AN ABSTRACT OF A MASTER'S THESIS

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## ABSTRACT

The base/solvent system consisting of potassium 3-methyl-3-pentoxide:3-methyl-3-pentanol (1:1) complex in triglyme was investigated for promoting elimination reactions with various alkyl tosylates and bromides. From exo-2-norbornyl tosylate a 77% yield of norbornene was observed, while exo-2-norbornyl bromide was converted to the olefin in 72% yield. Endo-2-norbornyl tosylate afforded norbornene exclusively although only in 10% yield. No nortricyclene was obtained in the above three reactions. Cyclopentyl tosylate and bromide produced cyclopentene in 60% and 64% yield, respectively, while cyclohexyl tosylate and bromide formed cyclohexene in 80% and 83% yield, respectively. 1-Pentyl tosylate and bromide were converted to 1-pentene in 68% and 61% yield, respectively. These yields were comparable with those derived from 1-hexyl tosylate and bromide where 1-hexene was formed in 66% and 62% yield, respectively. Reaction of the complex with 2-pentyl tosylate gave 57% yield of olefinic product which contained 76% 1-pentene and 24% trans-2-pentene. From 2-pentyl bromide, 54% yield of olefinic product was obtained containing 75% 1-pentene and 25% trans-2-pentene. From 3-pentyl tosylate and bromide, 2-pentene was formed in 54% and 53% yield, respectively.

All of the above reactions were carried out under identical conditions. The exclusive formation of norbornene from the exo- and endo-2-norbornyl derivatives is unusual.

The yields obtained are comparable to those from other methods. The important advantage of this base/solvent system is that the reactions can be carried out at room temperature in a solvent which does not promote ionization of the substrate.