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7/25/68

THE CHEMISTRY OF ALKYL N-CARBOALKOXYSULFAMATE ESTERS

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

by

Edward Alan Taylor

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Doctor of Philosophy

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THE CHEMISTRY OF ALKYL N-CARBOALKOXYSULFAMATE ESTERS

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Chairman

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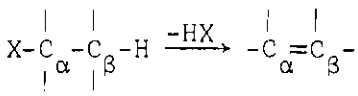
CHAPTER I

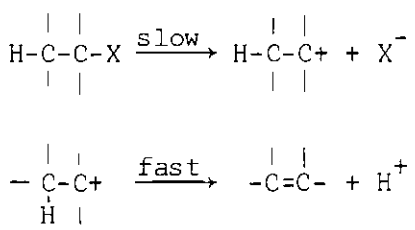
INTRODUCTION

One of the broadest classifications of reactions which introduce unsaturation in a molecule is the β-elimination in which the carbon designated α bears the leaving group, some nucleophile, X: and the carbon designated β has a proton removed.



β-Eliminations are classified according to the number of molecules involved in the transition state of the slow step and the timing of bond breaking during the reaction. On this basis three general types of mechanisms are recognized: E1, E2, and E1cB.

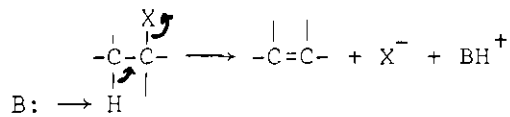
The E1 mechanism is a two-step process in which the rate determining step is unimolecular ionization of the substrate to give a carbonium ion which rapidly loses a β-proton to a base, usually the solvent.



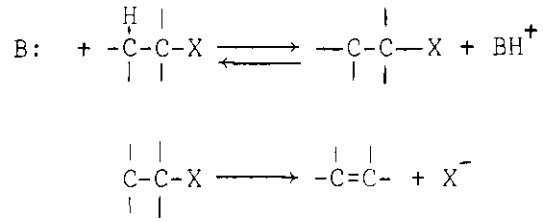
The E1 mechanism (1) is analogous to and competes with the Sn1 mechanism

since, in fact, the two mechanisms have a common intermediate. In the E1 mechanism the second step is removal by solvent of a β-proton rather than solvent capture at the positively charged carbon as in the substitution case. Since the olefin is formed from an intermediate ion, the yield and ratio of isomeric olefins should be independent of the leaving group (X^-) except in cases of ion-pairs or very low basicity media when the gegen-ion acts as the base for β-proton removal. Likewise, competing group rearrangements should be expected to arise when partial carbonium ions are involved.

In the E2 mechanism (elimination, bimolecular) the reaction takes place in one step and is kinetically second order (first order in base and substrate). In general it has been found that the E2 reaction is stereospecific with five atoms (including the base) lying in one plane with *trans*-stereochemistry.



The third mechanism, the E1cB or carbanion mechanism, has formation of a carbanion by base attack at the β-hydrogen as the rate determining step (3). This is followed by unimolecular ejection of X^- from the conjugate base.



This reaction pathway is most probably operable in cases of eliminations with β-carbons bearing nitro, cyano, keto, or other electron-withdrawing substituents which would greatly increase the acidity of the β-protons.

It is generally accepted that there is a spectrum of mechanisms ranging from E1 in which the leaving group departs first to E1cB in which the proton is lost first. The E2 case lies in the middle with simultaneous loss of both groups. The important question is which bond has undergone more cleavage in the transition state, C-H or C-X.

In addition to the detailed mechanisms there is the question of the direction of elimination. In the E1 mechanism initial loss of the leaving group results in product formation determined almost entirely by the relative hyperconjugative stabilities of the possible olefinic compounds. These cases are said to obey Saytzeff's rule which states that the predominant product of the reaction will be that in which the double bond involves the most highly substituted carbons.

For the E2 mechanism where *trans*,β-hydrogens are available on more than one carbon, the direction of elimination is almost entirely dependent on the leaving group. If the leaving group is positively charged, its electron-withdrawing effect makes differences in acidity of β-hydrogens more important. These cases are said to obey Hofmann's rule which states that the predominant product of the elimination will

involve removal of the most acidic and conformationally accessible β-proton which may result in the least highly substituted olefin. When the leaving group is a neutral species, this orientation is reversed and Saytzeff products are observed.

The yield of olefin from a reaction will largely depend upon how effectively the desired elimination competes with accompanying substitution reactions. The elimination/substitution ratio may depend on the identity or concentration of the attacking base, the polarity and temperature of the reaction medium, the structure of the substrate, or the nature of the leaving group.

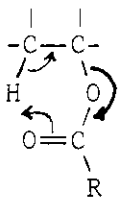
The identity of the attacking base is of lesser importance in E1 reactions but has considerable effect on the bimolecular reactions. If the base is weak but is strongly nucleophilic toward carbon, it will be very effective in bringing about bimolecular substitution but far less effective in bringing about bimolecular elimination. High concentrations and strong bases favor E2 over E1 and also enhance E2 over Sn2. Sterically hindered bases generally favor elimination over substitution.

With any reaction a more polar medium enhances the rate of reactions involving discrete ionic intermediates. Increasing solvent polarity favors Sn2 reactions at the expense of E2 and aids E1 and E1cB reactions having neutral leaving groups. Although most solvents favor Sn1 over E1 reactions, E1 predominates in polar solvents which are poor nucleophiles. Increasing temperature favors first or second order elimination over substitution.

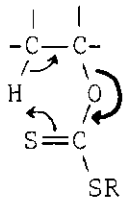
The substrate structure may have several effects on the reaction in that groups attached to either the α- or β-carbons may stabilize or destabilize the incipient double bond, carbanion, or carbonium ion.

As seen from previous discussion the nature of the leaving group has a marked effect on elimination reactions. The reactivity of the leaving group in eliminations is similar to nucleophilic substitution. The ability of a species to act as a leaving group is usually inversely proportional to its basicity, and the best leaving groups are generally the weakest bases. Better leaving groups favor the E1 mechanism since they result in less endothermic ionization. Positively charged leaving groups shift the mechanism toward the E1cB end of the spectrum and increase the amount of elimination vs. substitution in second order reactions. In first order reactions the leaving group has little effect on the competition between elimination and substitution except in cases involving ion-pairs in which product formation is affected by the nature of the leaving group (4).

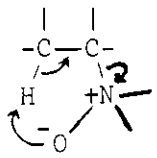
Certain classes of compounds (for example, carboxylic esters, xanthates, and amine oxides) will decompose to form olefins at elevated temperatures by mechanisms different from any previously discussed. These are pyrolytic eliminations, designated Ei (5), which have been shown to involve a *cis*, cyclic transition state in which a β-proton is removed intramolecularly by a basic atom which is part of the α-linked leaving group. In the cyclic transition states for esters (I), xanthates (II), and amine oxides (III) illustrated, the directions of electron transfer are based on the usual electronegativity of the atoms.



I



II

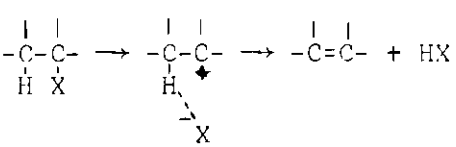


III

The completely *cis* nature of these eliminations has been demonstrated in cases where different geometrical isomers are formed dependent upon the stereochemical course of the elimination (6,7,8).

A whole spectrum of transition states with different degrees of bond forming and breaking is available for Ei reactions. At one extreme breakage of the C-X bond occurs first, in the middle both groups are lost simultaneously (pure E_i), and at the other extreme the C-H bond is first broken.

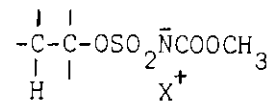
The case in which breakage of the C-X bond occurs first has the designation ion-pair mechanism. The leaving group ability is the paramount consideration in these cases. After the breakage of the C-X bond, the newly formed gegen-ion attacks the β-proton resulting in olefin formation. This mechanism is especially important in cases of reaction with good leaving groups in non-polar media.



As is the case with the general E1 elimination, the better the

leaving group the greater the ease of ionization. In a *cis*-elimination involving an ion-pair mechanism, the most facile reaction should be that in which the leaving group ionizes easily, i.e., the C-X bond is the weakest. Carboxylic esters, xanthates, amine oxides, halides, or *p*-toluenesulfonates all require elevated temperatures and/or strong acid or base to undergo elimination.

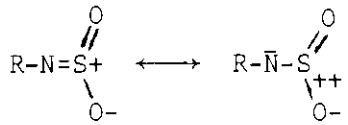
The studies reported in this thesis are concerned with the investigation of a new leaving group, alkyl N-carbomethoxysulfamate salts (IV).



IV

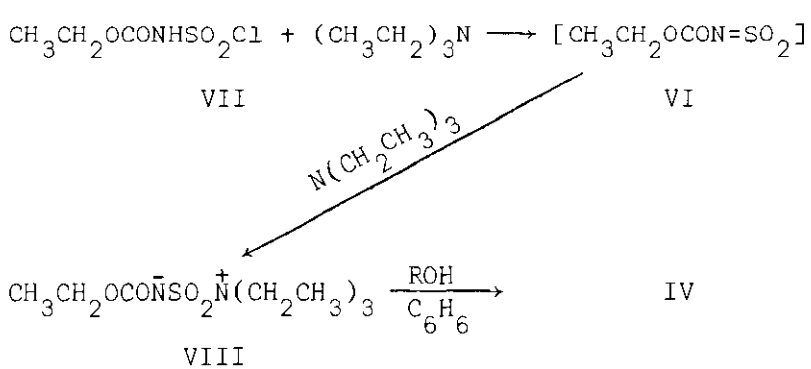
$X^+ = (CH_3CH_2)_3NH^+, Na^+$

These compounds are derived from the recently synthesized heterocumulenes, N-sulfonylamines (V) (9), which have been shown to undergo various cycloaddition reactions with nucleophilic olefins and attack bases such as amines and alcohols. This heterocumulene might be expected to exhibit such reactivity due to a polarization of the nitrogen-sulfur double bond. This polarization is caused by the differences in electronegativity among the atoms of the cumulene system.

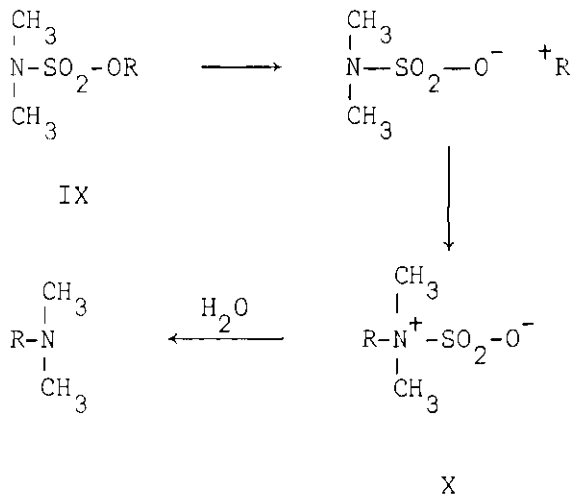


V

N-Carboethoxysulfonylamine (VI) was prepared by the action of triethylamine on carboethoxysulfamoyl chloride (VII). When VII was treated with two moles of triethylamine in benzine, filtration of triethylamine hydrochloride and removal of solvent resulted in a white crystalline solid, (carbosulfamoyl)triethylammonium hydroxide, inner salt, ethyl ester (VIII). In solution VIII participates in a rapid equilibrium forming VI and triethylamine. If a benzene solution of VIII is allowed to react with an alcohol, nucleophilic attack of the alcohol oxygen on the sulfur atom results in an adduct which then undergoes deprotonation with the triethylamine present to form IV.

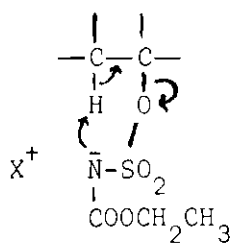


White and Elliger (10) had previously demonstrated the conversion of alcohols to tertiary amines *via* the Sn_i rearrangement of N,N-dialkylsulfamate esters (IX)

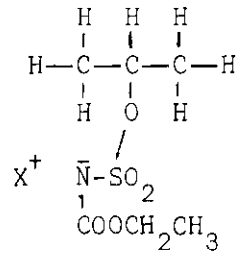


The reaction is described as occurring by initial cleavage of the oxygen-carbon bond followed by nucleophilic attack of nitrogen on the carbonium ion (R^+) resulting in the zwitter-ionic species (X) which when hydrolyzed formed the tertiary amine. Traube, Zander, and Gaffron (11) have reported similar conversions of methyl, ethyl, and benzyl N,N-dialkylsulfamates.

Carboalkoxysulfamate esters contain a carbonyl function adjacent to nitrogen in contrast to simple alkylsulfamate esters. It might be expected that compared to the dialkyl cases the inductive effect of the carboalkoxy group would result in a much better leaving group which would lower the energy of the ionization step in the elimination reaction. A *cis,* cyclic, six-centered transition state (XI) could be pictured for this elimination (12).



XI



XII

Significantly, when 2-propyl N-carboethoxy-sulfamate, triethylammonium salt (XII) was warmed in benzene (13), propene was evolved from the reaction mixture.

Synthetic interest in this facile olefin formation arises from the facts that this sulfamate derivative was easily formed and appeared to eliminate at low temperatures in a non-polar medium.

The purpose of this research was to determine the scope and synthetic utility of alkyl-N-carbomethoxysulfamate thermolyses and to explore the mechanism of this reaction.

CHAPTER II

EXPERIMENTAL

Apparatus and Techniques

Anhydrous benzene was distilled from sodium and stored over sodium ribbon. Tetrahydrofuran was distilled from lithium aluminum hydride before use. Triethylamine and acetonitrile were dried by distillation from powdered phosphorus pentoxide. Dimethylformamide was dried and stored over molecular sieves. Methanol was distilled from magnesium methoxide prior to use.

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Elemental microanalyses were performed by Huffman Laboratories, Wheatridge, Colorado.

Nuclear magnetic resonance spectra were obtained using a Varian, Model A-60D, spectrometer with tetramethylsilane used as an internal standard. Chemical shifts are reported in units of τ ($\tau = 10 - \delta$) and the abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively. For a multiplet a single value for the chemical shift is given which is the center of gravity of the multiplet. In cases of multiplets whose centers of gravity are not easily discerned the chemical shifts are reported as a range.

Mass spectral data were obtained using a Varian, Model 66, mass spectrometer. Ultraviolet spectra were obtained from a Cary Model 14 recording spectrophotometer using one centimeter quartz cells and

95 per cent aqueous ethanol as solvent. Infrared spectra were obtained on a Perkin Elmer 457 spectrophotometer.

Gas-liquid phase chromatography was performed using an Fand M, Model 700, dual column gas chromatograph fitted with a silicon rubber column (four feet) with helium as the carrier gas, for collection of analytical samples. General analytical data were obtained using a Hewlett-Packard, Model 402, dual column gas chromatograph fitted with a Ucon polar column (four feet) using nitrogen as the carrier gas.

The apparatus used in the thermolyses consisted of a U-shaped glass tube with standard taper glass joints at each end. At the end to be inserted into the reaction vessel was a gas inlet tube which admitted a flow of nitrogen. The other end of the U-tube was fitted to a dry-ice and acetone cold trap.

The format used in reporting physical data of compounds follows that recommended for American Chemical Society journals (14).

Kinetic Data

Kinetic data for 1,2-diphenylethyl-N-carbomethoxysulfamate triethylammonium salt (XIII), *erythro*-2-deuterio-1,2-diphenylethyl-N-carbomethoxysulfamate triethylammonium salt (XIV), and *threo*-2-deuterio-1,2-diphenylethyl-N-carbomethoxy sulfamate triethylammonium salt (XV) (15) were obtained spectrophotometrically with a Cary 14 spectrophotometer by placing solutions of XIII, XIV, and XV in the beam-path sample compartment in which the temperature was maintained ±0.3°C by a constant temperature water bath. The progress of the reaction was measured by the development of stilbene absorption at 295 nm as a function of time.

(Carboxysulfamoyl)triethylammonium Hydroxide, Inner Salt, Methyl Ester

Carbomethoxysulfamoyl Chloride (XVI)

Anhydrous methanol (18.80 g, 0.550 mole) in 25 ml of benzene was added dropwise to a solution of chlorosulfonyl isocyanate (16) (65.72 g, 0.500 mole) and 200 ml of benzene in a 500 ml flask fitted with a 50 ml addition funnel. The mildly exothermic reaction was controlled with a cool water bath. After the addition was complete (30 minutes), the solvent and excess methanol were removed from the reaction mixture under reduced pressure. The resulting white crystalline mass was crystallized from toluene to give colorless needles (61.00 g, 91.9%) of carbomethoxysulfamoyl chloride (XVI): mp 70-71°C.

Anal. Calcd for $C_2H_4ClNO_2S$: C, 13.88; H, 2.33; N, 8.10; S, 18.49. Found: C, 13.76; H, 2.53; N, 8.13; S, 18.72.

(Carboxysulfamoyl)triethylammonium, Hydroxide, Inner Salt, Methyl Ester (XVII)

Carbomethoxysulfamoyl chloride (XVI) (3.47 g, 0.020 mole) dissolved in 50 ml of benzene was added dropwise to a solution of triethylamine (4.60 g, 0.045 mole) and 25 ml of benzene in a 250 ml three-neck round-bottom flask fitted with a 125 ml addition funnel under a nitrogen atmosphere at ambient temperature. After the addition was complete (one hour), the precipitate of triethylamine hydrochloride (0.56 g, 96 per cent theoretical) was removed by filtration, and the solvent was evaporated under reduced pressure to afford a residual colorless oil which solidified on standing. Crystallization from toluene yielded colorless needles (3.87 g, 81%) of (carboxysulfamoyl)triethyl-

ammonium, hydroxide, inner salt, methyl ester (XVII): mp 71-72°C; nmr ($CDCl_3$) τ 6.34 (s, 3H), 6.71 (q, 6H, J = 7Hz), and 8.85 (t, 9H, J = 7 Hz).

Anal. Calcd for $C_8H_{18}N_2O_4S$: C, 40.32; H, 7.62; N, 11.72; S, 13.43. Found: C, 40.04; H, 7.54; N, 11.51; S, 13.36.

Preparation of Substrates

Endo-2-Methyl-[2.2.1.]-bicycloheptan-2-ol (XVIII)

Methyl iodide (11.36 g, 0.08 mole) dissolved in 25 ml of anhydrous diethyl ether was added dropwise to a mechanically stirred suspension of magnesium turnings (1.82 g, 0.075 mole) in 25 ml of diethyl ether. The resulting solution was treated dropwise with norcamphor (5.50 g, 0.05 mole) dissolved in 25 ml of diethyl ether. After this addition was complete (15 minutes), the reaction mixture was allowed to stir for one hour after which it was hydrolyzed with a saturated aqueous solution of ammonium chloride and extracted with three 10 ml portions of diethyl ether. The ether layer was separated, dried over anhydrous sodium sulfate and evaporated to yield colorless prisms (5.51 g, 89%) of *endo*-2-methyl-[2.2.1.]-bicycloheptan-2-ol (XVIII): mp 30-31°C (lit. (17) 31.5-32°C); is ($CHCl_3$) 3620 (O - H), 2950, and 2870 cm^{-1}, no C = O band; nmr ($CDCl_3$) τ 7.27 (s, 1 H), 8.32 (complex m, 10 H), 8.70 (s, 3 H).

3-*t*-Butyl-2,2,4-trimethyl-pentan-3-ol (XIX)

A solution of 1.7 M *t*-butyl lithium (122 ml, 10.01 g, 0.16 mole) in pentane in a 500 ml three-neck round-bottom flask fitted with a 125 ml addition funnel under a nitrogen atmosphere was cooled to -78°C with

a dry-ice and acetone bath. Ethyl 2-methyl-propanoate (8.13 g, 0.07 mole) in 50 ml of diethyl ether was added dropwise and the reaction mixture was allowed to stir for one hour at -78°C. After allowing the reaction to warm to room temperature, the excess τ-butyl lithium was destroyed by the slow addition of water. The reaction was neutralized with 30 per cent aqueous hydrochloric acid and extracted three times with 25 ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to yield a colorless oil which crystallized on standing. Crystallization from benzene-hexane gave colorless needles (12.37 g, 95%) of 3-*t*-butyl-2,2,4-trimethyl-pentan-3-ol (XIX): mp 24-25°C; ir ($CHCl_3$) 3620 (O-H), 2950, 2920, and 2880 cm^{-1}, no C = O band; nmr ($CDCl_3$) τ 6.42 (s, 1H), 8.08 (m, 1H, J = 7 Hz), 8.98 (d, 6H, J = 7 Hz), 9.08 (s, 18H); mass spectrum, molecular ion, theoretical 186.340, found 186.342.

Thermolyses of Tertiary Alkyl Sulfamate Esters

Endo-2-Methyl-[2.2.1]-bicycloheptan-2-ol (XVIII)

Endo-2-Methyl-[2.2.1]-bicycloheptan-2-ol (XVIII) (4.20 g, 0.032 mole) in 10 ml of acetonitrile was added dropwise to a solution of XVII (9.00 g, 0.038 mole) and 20 ml of acetonitrile in a 50 ml round-bottom flask fitted with a reflux condenser and calcium chloride drying tube. The temperature was raised to 50°C and maintained for one hour after which the reaction mixture was cooled, treated with 15 ml of water, and extracted with three 10 ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to give

a colorless liquid (2.76 g, 80%) which was shown by glc to contain two components.

Separation was affected by collection from a gas-liquid chromatograph (20% carbowax column, injector temperature 220°C, detector temperature 220°C, column temperature 65°C). The peak of shorter retention time (47% of the mixture) was identified as 2-methyl-[2.2.1]-bicyclohept-2-ene (XX): nmr (18) ($CDCl_3$) τ 4.58 (m, 1H), 7.29 (m, 1H), 7.46 (m, 1H), 8.32 (d, 3H, J = 2 Hz); mass spectrum, molecular ion, theoretical 108.172, found, 108.169. The other component was identified as 2-methylene-[2.2.1]-bicycloheptane (XXI): nmr (19) ($CDCl_3$) τ 5.22 (m, 1H), 5.48 (m, 1H), 7.34 (M, 1H), 7.67 (m, 1H), 8.00 (m, 1H); mass spectrum, molecular ion, theoretical 108.172, found, 108.173.

3-*t*-Butyl-2,2,4-trimethyl-pentan-3-ol (XIX)

3-*t*-Butyl-2,2,4-trimethyl-pentan-3-ol (XIX) (3.00 g, 0.016 mole) in 10 ml of acetonitrile was added dropwise to a solution of XVII (4.75 g, 0.020 mole) and 25 ml of acetonitrile in a 50 ml round-bottom flask fitted with a reflux condenser. The temperature was raised to 50°C and maintained for one hour after which the reaction was cooled, treated with water, and extracted three times with 10 ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to afford a colorless liquid (1.88 g, 70%) which was shown by glc to be homogeneous and was subsequently identified as 3-*t*-butyl-2,3,4-trimethyl-pent-1-ene (XXII): ir ($CHCl_3$) no O-H band, 2950, 2930, 2890, and 1645 cm^{-1} (C = C); nmr ($CDCl_3$) τ 5.10 (m, 1 H), 5.18 (m, 1 H), 8.08 (h, 1 H, J = 7 Hz), 8.20 (d, 3H, J = 2 Hz), 8.97 (d, 6 H,

J = 7 Hz), 9.03 (s, 3H), 9.08 (s, 9H); mass spectrum (70 eV) m/e (relative intensity) 168 (1.0), 112 (100), 97 (95), 69 (90), 57 (85), 43 (65), 41 (83).

2-Methyl-butan-2-ol (XXIII)

2-Methyl-butan-2-ol (XXIII) (2.30 g, 0.025 mole) was added neat to XVII (7.50 g, 0.032 mole) at ambient temperature in a 50 ml round-bottom flask connected to a cold trap by a glass U-tube (see apparatus). Within five minutes of the addition an exothermic reaction developed and the reaction mixture became homogeneous. A clear colorless liquid distilled into the cold trap. The reaction mixture was flushed with a stream of dry nitrogen for one hour after which the collected distillate was analyzed by glc. The colorless liquid (2.00 g, 95%) was shown to be a mixture of 2-methyl-2-butene (70%) (XXIV) and 2-methyl-1-butene (30%) (XXV) (20).

Dimethylcyclopropyl Carbinol (XXVI)

Dimethylcyclopropyl carbinol (XXVI) (21) (3.00 g, 0.034 mole) was added neat to XVII (9.50 g, 0.040 mole) in a 50 ml round-bottom flask connected to the thermolysis apparatus at ambient temperature under a stream of dry nitrogen. After ten minutes an exothermic reaction ensued and the reaction mixture became homogeneous. A clear colorless liquid distilled into the cold trap. Glc analysis of the liquid (1.20 g, 66% showed one component which was identified as 2-cyclopropylpropene (XXVII): nmr ($CDCl_3$) τ 5.33 (m, 2H), 8.36 (d, 3H), 8.90 (complex t, 1H), 9.43 (m, 4H); mass spectrum, molecular ion, theoretical 82.147, found, 82.144.

3,4-Epoxy-2-methyl-butan-2-ol (XXVIII)

3,4-Epoxy-2-methyl-butan-2-ol (XXVIII) (22) (3.00 g, 0.029 mole) was added neat to XVII (9.50 g, 0.040 mole) in a 50 ml round-bottom flask connected to the thermolysis apparatus at ambient temperature under a stream of dry nitrogen. The reaction mixture was warmed to 55°C for several minutes while a rapid distillation of a clear colorless liquid into the cold trap occurred. Glc analysis of the distillate (1.41 g, 69%) showed one component which was subsequently identified as 3,4-epoxy-2-methyl-but-1-ene (XXIX) (23): nmr ($CDCl_3$) τ 4.83 (m, 1H, J = 1 Hz), 6.65 (m, 1H, J = 3 Hz), 7.25 (complex m, 2H, J = 3 Hz), 8.37 (d, 3H, J = 2 Hz); mass spectrum, molecular ion, theoretical 84.119, found, 84.120.

Phenol (XXX)

Phenol (XXX) (1.88 g, 0.020 mole) was added neat to XVII (5.00 g, 0.021 mole) in a 50 ml round-bottom flask connected to the thermolysis apparatus at ambient temperature under a stream of dry nitrogen. A vigorous exothermic reaction resulted in a homogeneous reaction mixture. The temperature was raised to 200°C and even at reduced pressure no distillation occurred. The reaction mixture was cooled, treated with 20 ml of water, and extracted three times with 10 ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to afford only starting material (20).

In another example, XXX (1.88 g, 0.020 mole) was added neat to XVII (5.00 g, 0.021 mole) as before. The reaction mixture was dissolved in 20 ml of dry tetrahydrofuran and treated with sodium hydride (0.48 g,

0.020 mole). The solvent was evaporated and the resulting white solid was thermolyzed at 200°C with no difference from the previous result.

Thermolyses of Secondary Alkyl Sulfamate Esters

Cyclohexanol (XXXI)

Cyclohexanol (XXXI) (4.30 g, 0.043 mole) in 10 ml of freshly distilled tetrahydrofuran was added dropwise to a solution of XVII (10.70 g, 0.045 mole) and 20 ml of tetrahydrofuran in a 50 ml round-bottom flask connected to the distillation apparatus at ambient temperature under a stream of dry nitrogen. The reaction mixture was treated with sodium hydride (1.03 g, 0.043 mole), prepared from 1.75 g of sodium hydride/mineral oil dispersion by several washings with dry hexane, and maintained at ambient temperature until hydrogen evolution ceased. The temperature was raised to 50°C and a clear colorless liquid distilled into the cold trap. Glc analysis of the distillate (2.92 g, 83%) showed one component which was identified as cyclohexene (XXXII) (20).

3,3-Dimethyl-butan-2-ol (XXXIII)

3,3-Dimethyl-butan-2-ol (XXXIII) (3.00 g, 0.029 mole) in 5 ml of triglyme was added dropwise to a solution of XVII (7.50 g, 0.032 mole) and 25 ml of triglyme in a 50 ml round-bottom flask connected to the thermolysis apparatus at ambient temperature under a stream of dry nitrogen. The reaction mixture was treated with sodium hydride (0.77 g, 0.032 mole), prepared from 1.35 g of sodium hydride/mineral oil dispersion by several washings with dry hexane, and maintained at ambient temperature until hydrogen evolution ceased. The temperature was raised

to 60°C and a clear colorless liquid distilled into the cold trap. Glc analysis of the distillate showed three components which were identified as 3,3-dimethyl-but-1-ene (XXXIV) (18%), 2,3-dimethyl-but-2-ene (XXXV) (55%), and 2,3-dimethyl-but-1-ene (XXXVI) (27%) (20). The total yield of olefinic products was 2.28 g, 85%.

In another example the reaction as described above was run using benzene as a solvent. The distillate had the same components in slightly different proportion: XXXIV (19%), XXXV (58%), and XXXVI (23%). The total yield of olefinic products was 2.25 g, 84%.

In yet another example tetrahydrofuran was used as the solvent. After hydrogen evolution had ceased, solvent was removed *in vacuo* to yield a white solid which when heated to 100°C yielded a clear colorless distillate with the composition: XXXIV (16%), XXXV (65%), and XXXVI (20%). The total yield of olefinic products was 2.30 g, 86%.

[2.2.2.]-Bicyclooctan-2-ol (XXXVII)

[2.2.2.]-Bicyclooctan-2-ol (XXXVII) (2.20 g, 0.018 mole) in 10 ml of benzene was added dropwise to a solution of XVII (6.00 g, 0.025 mole) and 25 ml of benzene in a 50 ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. After the addition was complete (20 minutes), the temperature was raised to 60°C and maintained 30 minutes after which 10 ml of water was added. The benzene layer was separated, dried over anhydrous

sodium sulfate, and evaporated to give white plates (1.68 g, 89 per cent) of [2.2.2.]-bicyclooct-2-ene (XXXVIII): mp 113°C (lit. (25) 113-114°C) (20).

4-Hexen-3-ol (XXXIX)

4-Hexen-3-ol (XXXIX) (4.38 g, 0.044 mole) was added to XVII (10.70 g, 0.045 mole) in 25 ml triglyme in a 50 ml round-bottom flask connected to the thermolysis apparatus at ambient temperature under a stream of dry nitrogen. The temperature was raised to 75°C and a clear colorless liquid distilled into the cold trap. Glc analysis of the distillate (2.62 g, 73%) showed one component which was identified as 2,4-hexadiene (XL) (20).

In another example, XXXIX (3.00 g, 0.030 mole) in 10 ml of tetrahydrofuran was added dropwise to a solution of XVII (7.50 g, 0.032 mole) and 20 ml of tetrahydrofuran in a 50 ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. After the addition was complete (20 minutes) the reaction mixture was treated with sodium hydride (0.72 g, 0.030 mole), prepared from 1.27 g of sodium hydride/mineral oil dispersion by several washings with dry hexane, and maintained at ambient temperature until hydrogen evolution had ceased. The solvent was removed under reduced pressure to afford a white solid which was heated at 80°C for 30 minutes. Water (10 ml) was added and the reaction was extracted three times with 10 ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to give a pale yellow oil (2.28 g, 94%) which glc showed to be one component, and was

subsequently identified as methyl N-2-hex-3-enylcarbamate (XLI): ir ($CHCl_3$) 3440 (N-H), 2960, 2900, 1720 (O-CO-N), and 1675 cm^{-1} (C = C); nmr ($CDCl_3$) τ 4.45 (complex m, 2H), 5.90 (broad s, 1H), 6.40 (s, 3H), 8.00 (complex m, 1H), 8.35 (m, 2H), 8.95 (m, 6H); mass spectrum, molecular ion, theoretical 157.215, found, 157.217.

1,2-Diphenylethanol (XLII)

1,2-Diphenylethanol (XLII) (3.96 g, 0.020 mole) (26) in 15 ml of benzene was added dropwise to a solution of XVII (5.00 g, 0.021 mole) and 20 ml of benzene in a 50 ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. After the addition was complete (30 minutes), the temperature was raised to 50°C and maintained for 30 minutes. Water (10 ml) was added and the benzene layer was separated, dried over anhydrous sodium sulfate, and evaporated to yield a white crystalline solid. Crystallization from ethanol gave colorless plates (3.42 g, 95%) of *trans*-stilbene (XLIII): mp 124°C (lit. (27) 124°C) (20). In another example, the reaction was repeated in exact proportions using N,N-dimethylformamide as the solvent. After maintaining the temperature at 50°C for 30 minutes, water (10 ml) was added and the reaction mixture was extracted three times with 10 ml portions of ether. The ether extracts were combined, washed three times with 25 ml portions of water, dried over anhydrous sodium sulfate, and evaporated to afford a white crystalline solid. Crystallization from ethanol gave 3.45 g (96%) of pure XLIII (20).

Erythro-2-Deuterio-1,2-Diphenylethanol (XLIV)

The same procedure for XLII was carried out using XLIV (6) (3.36 g, 0.017 mole) in 10 ml of benzene and XVII (4.30 g, 0.018 mole) in 20 ml of benzene. Recrystallization from ethanol gave colorless plates (2.89 g, 94%) of α-deuterio-*trans*-stilbene (XLV): mp 124°C (lit. (28) 124°C); nmr ($CDCl_3$) τ 2.65 (m, 10H), 3.01 (s, 1H); mass spectrum (70 eV) m/e (relative intensity) 182 (14), 181 (97), 180 (100). For pure XLIII: mass spectrum (70 eV) m/e (relative intensity) 181 (14), 180 (100). For XLV the minimum deuterium atom/molecule, 0.97.

In another example, the reaction was repeated in exact proportions using N,N-dimethylformamide as the solvent. Using the same work-up as for XLII in N,N-dimethylformamide, 2.91 g (95%) pure XLV was obtained.

Threo-2-Deuterio-1,2-diphenylethanol (XLVI)

The same procedure for XLII was carried out using XLVI (6) (3.36 g, 0.017 mole) in 10 ml of benzene and XVII (4.30 g, 0.018 mole) in 20 ml of benzene. Recrystallization from ethanol gave 2.83 g (92%) of pure XLIII (20).

In another example, the reaction was carried out in exact proportions using N,N-dimethylformamide as the solvent. Again, using the same work-up as for XLII in this solvent, 2.86 g (93%) of pure XLIII (20) was obtained.

Thermolyses of Primary Alkyl Sulfamate Esters

1-Hexanol (XLVII)

1-Hexanol (XLVII) (3.00 g, 0.029 mole) was added neat to XVII (7.40 g, 0.031 mole) in a 50 ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. After a mild exothermic reaction, the viscous yellow oil was heated to 95°C for 30 minutes. Water (10 ml) was added and the reaction mixture was extracted three times with 10 ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to yield 4.25 g (91%) of a colorless oil which was identified as methyl N-hexylcarbamate (XLVIII) (20).

In another example, XLVII (1.96 g, 0.019 mole) was added neat to XVII (5.00 g, 0.021 mole) at ambient temperature under an atmosphere of nitrogen. After the mild exothermic reaction had ceased, the reaction mixture was dissolved in 20 ml of benzene and rapidly washed with a cold aqueous solution of 2 per cent hydrochloric acid. The benzene layer was separated, dried over anhydrous sodium sulfate and evaporated to give a viscous golden oil: ir ($CHCl_3$) 3325 (N-H), 3000, 1740 (C = O), 1330 and 1160 cm^{-1} (SO_2-N); nmr ($CDCl_3$) τ 1.85 (broad s, 1H), 5.70 (t, 2H), 6.30 (s, 3H), 8.75 (m, 8H), 9.10 (t, 3H).

When placed in the thermolyses apparatus and subjected to a temperature of 150°C, the neat oil gave a clear colorless distillate which on glc analysis showed two components: 1-hexene (XLIX) (50%) and 2-hexene (L) (50%) (20). The total yield of olefinic products was 1.14 g (70%).

Benzyl Alcohol (LI)

Benzyl alcohol (LI) (2.16 g, 0.020 mole) was added neat to XVII (5.95 g, 0.025 mole) in a 50 ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. The resulting exothermic reaction produced a homogeneous reaction mixture. Reducing the pressure to 0.5 torr and raising the temperature to 115°C distilled a pale yellow liquid (2.64 g, 80%) which was identified as methyl-N-benzylcarbamate (LII) (20).

2,2-Dimethyl-propan-1-ol (LIII)

2,2-Dimethyl-propan-1-ol (LIII) (1.76 g, 0.020 mole) in 10 ml of benzene was added dropwise to a solution of XVII (5.95 g, 0.025 mole) and 20 ml of benzene in a 50 ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. The benzene was removed under reduced pressure and the residue dissolved in 25 ml of tetrahydrofuran. The solution was treated with sodium hydride (0.53 g, 0.022 mole), prepared from 0.93 g of sodium hydride/mineral oil dispersion by several washings with dry hexane, and maintained at ambient temperature until hydrogen evolution had ceased. The tetrahydrofuran was evaporated to yield a white solid which was thermolyzed at 110°C for 30 minutes. A clear colorless liquid distilled (1.17 g, 84%) which was identified as 2-methyl-2-butene (XXIV) (20).

Syn-Benzaldehyde Oxime (LIV)

Syn-Benzaldehyde oxime (LIV) (2.42 g, 0.020 mole) was added neat to XVII (5.00 g, 0.021 mole) in a 50 ml round-bottom flask fitted with a

reflux condenser at ambient temperature under an atmosphere of dry nitrogen. After an exothermic reaction, the viscous oil was heated to 90°C for 30 minutes, cooled, dissolved in 20 ml of benzene, washed once with 10 ml of a saturated aqueous sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated to yield 1.36 g (57%) of formanilide (LV): mp 45°C (lit. (29) 43°C) (20).

Other Leaving Groups

p-Toluenesulfonyl Isocyanate

Cyclohexanol (XXXI) (2.00 g, 0.020 mole) was added neat to *p*-toluenesulfonyl isocyanate (4.00 g, 0.020 mole) in a 50 ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. After the exothermic reaction subsided, the viscous oil was dissolved in 10 ml of tetrahydrofuran and treated with sodium hydride (0.48 g, 0.020 mole), prepared from 0.84 g of sodium hydride/mineral oil dispersion by several washings with dry hexane, and maintained at ambient temperature until hydrogen evolution had ceased. The tetrahydrofuran was evaporated and the resulting white solid was thermolyzed at 100°C. The contents of the reaction vessel slowly darkened to a black semi-solid, but no olefin distilled.

Phenyl Isocyanate

In a manner similar to that described for *p*-lotuenesulfonyl isocyanate, cyclohexanol (XXXI) (2.00 g, 0.020 mole) was treated with phenyl isocyanate (2.38 g, 0.020 mole) and sodium hydride (0.48 g, 0.020 mole). No reaction occurred on heating the salt overnight at 150°C (12).

N-Sulfinyl Acetamide

In a manner similar to that described for *p*-toluenesulfonyl isocyanate, cyclohexanol (XXXI) (6.00 g, 0.060 mole) was treated with N-sulfinyl acetamide (30) (6.30 g, 0.060 mole) and sodium hydride (1.44 g, 0.060 mole). After heating at 100°C for 6 hours the contents of the reaction vessel had become an amorphous brown semi-solid. No olefin distilled.

Dicyclohexylcarbodiimide

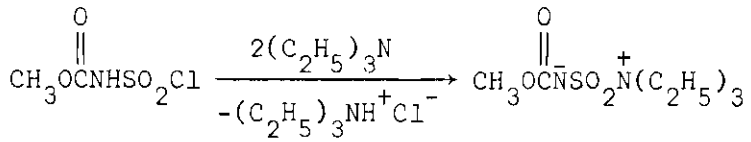
Cyclohexanol (XXXI) (2.00 g, 0.020 mole) was treated with sodium hydride (0.48 g, 0.020 mole) in 15 ml of dry tetrahydrofuran in a 50 ml round-bottom flask under an atmosphere of dry nitrogen. This solution was added to dicyclohexylcarbodiimide (4.12 g, 0.020 mole) and the tetrahydrofuran evaporated to yield a clear yellow oil which underwent no change on heating at 100°C for 6 hours.

CHAPTER III

DISCUSSION OF RESULTS

The purpose of this research was to determine the scope, mechanism, and synthetic utility of alkyl N-carbomethoxysulfamate ester thermal decompositions. This was accomplished by the investigation of products formed from a number of thermolyses of sulfamate esters derived from a series of alcohols with varying electronic and structural features.

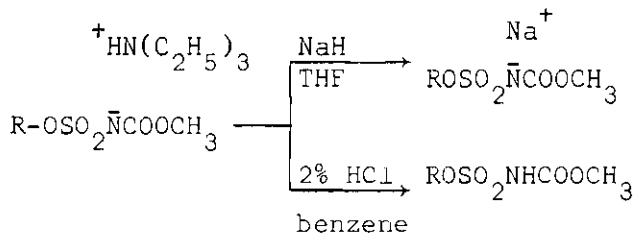
In the interest of simplifying nmr analysis and in determination of the generality of N-sulfonylamine preparations, (carboxysulfamoyl) triethylammonium hydroxide, inner salt, methyl ester (XVII) was prepared from carbomethoxysulfamoyl chloride (XVI) in the same manner as ethyl ester (VIII) had been prepared from carboethoxysulfamoyl chloride (VII) (9). When XVI was added to a benzene solution containing two equivalents of triethylamine at room temperature, a quantitative yield of triethylamine hydrochloride precipitated and was removed by filtration. The benzene solution yielded colorless needles which analyzed for the N-sulfonylamine-triethylamine adduct (XVII).



XVI XVII

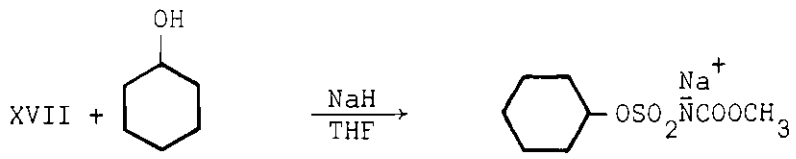
The structure of XVII was established by examination of its infrared and nmr spectra noting the analogy to previously identified VIII. The infrared spectrum showed no bands characteristic of N-H bonds and the carbonyl stretching frequency occurred at 1685 cm^{-1}, identical to that of VIII. The nmr spectrum showed absorptions for one O-methyl group [singlet (3H) at τ 6.34] and for three equivalent N-ethyl groups [quartet (6H) at τ 6.71 and triplet (9H) at τ 8.85].

In addition, XVII reacted with alcohols to form alkyl N-carbomethoxysulfamate esters (IV). The triethylammonium gegenion of these sulfamate esters was readily exchanged for either a sodium cation or a proton. If a dry tetrahydrofuran solution of an alkyl N-carbomethoxysulfamate triethylammonium salt was treated with one equivalent of sodium hydride and the solvent and liberated triethylamine evaporated, an infusible sulfamate ester sodium salt was obtained. The free base resulted from rapid washing of a benzene solution of the triethylammonium salt with a cold 2 per cent aqueous hydrochloric acid solution.

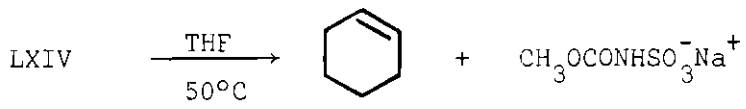


The reaction of VIII with isopropyl alcohol had been shown to result in isopropyl N-carboethoxysulfamate triethylammonium salt (XII) which when heated to 60°C resulted in ethyl carbamate and two unidentified volatile compounds assumed to be sulfur trioxide and propene (13).

When a dry tetrahydrofuran solution of XVII was treated with cyclohexanol (XXXI) and sodium hydride, and the resulting homogeneous mixture heated to 50°C while being swept with dry nitrogen, cyclohexene (XXXII) distilled from the reaction mixture. Remaining in solution was the inorganic salt (LVI) which was isolated as a white crystalline substance by sublimation and gave methyl carbamate on hydrolysis.

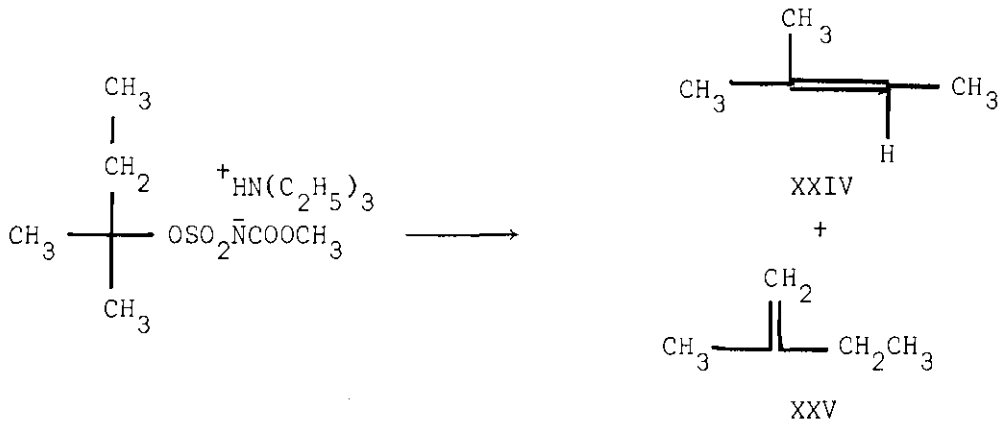


XXXI LXIV



XXXII LVI

The elimination was applied to 2-methyl-2-butanol (XXIII) to determine whether the elimination more closely obeyed the Hofmann or Saytzeff rule. Treatment of XXIII with XVII neat at room temperature afforded a 2·4:1 (glc) mixture of 2-methyl-2-butene (XXIV) and 2-methyl-1-butene (XXV), indicating a predominance of the more substituted Saytzeff product. The ratio of XXIV:XXV is smaller than that obtained from the elimination of the corresponding tosylates (31).



To determine the effect of solvent on the elimination, 3,3-dimethyl-2-butanol (XXXIII) was reacted with XVII followed by sodium hydride to form its sulfamate ester sodium salt which was subsequently thermolyzed to give 3,3-dimethyl-1-butene (XXXIV), 2,3-dimethyl-2-butene (XXXV), and 2,3-dimethyl-1-butene (XXXVI). Table 1 shows the results from carrying out these thermolyses in triglyme, benzene, and as a neat solid. The effect of solvent on the product ratios of the elimination in aliphatic cases appears to be negligible.

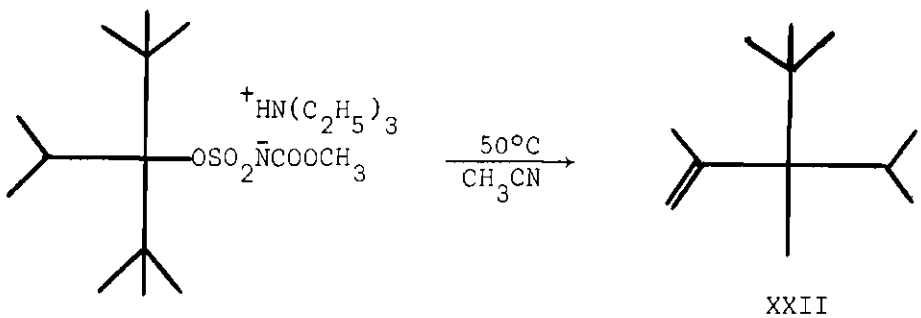
Table 1. Thermolyses of 3,3-Dimethyl-2-Butyl-N-Carbomethoxysulfamate Sodium Salt

Temperature (°C)	Solvent	Products (Ratio) XXXIV	XXXV	XXVI
60	triglyme	1	3	1.2
70	benzene	1	3	1.5
100	neat	1	4	1.2

In all cases the favored products are the result of methyl migration to the developing neopentyl carbonium ion. The amount of unrearranged material is surprising since the competition between Meerwein rearrangement and β-proton removal usually lies completely in the direction of the former (32).

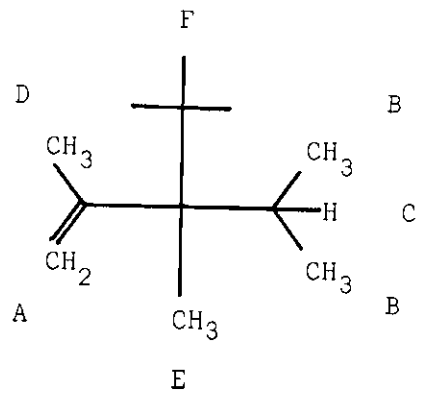
3-*t*-Butyl-2,2,4-trimethyl-3-pentanol (XIX) was prepared by treating ethyl isobutyrate with two equivalents of *t*-butyl lithium in pentane at -78°C. The structure of XIX was determined by its infrared and nmr spectra and mass spectral data. The infrared showed O-H bond stretching frequency at 3620 cm^{-1} and no bands characteristic of C=O bonds. The nmr spectrum showed absorptions for O-H [singlet (1H) at τ 6.42], for one isopropyl group [multiplet (1H) at τ 8.08 and doublet (6H) at τ 8.98] and for two equivalent *t*-butyl groups [singlet (18H) at τ 9.08]. The theoretical exact mass is 186.340 as compared to the experimentally determined value of 186.342.

When XIX was reacted with XVII in acetonitrile and heated to 50°C, the result was 3-*t*-butyl-2,3,4-trimethyl-1-pentene (XXII) as the only product.



XXII

The structure of XXII was determined by infrared, nmr, and mass spectral data. The infrared spectrum contained no bands characteristic of O-H bonds but had an absorption at 1645 cm^{-1} characteristic of a terminal carbon-carbon double-bond. The nmr spectrum showed the following:

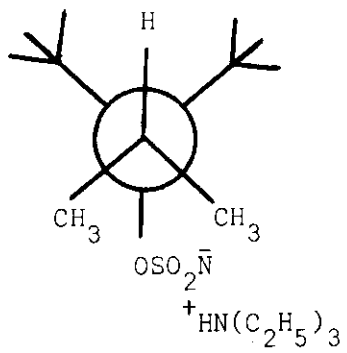


XXII

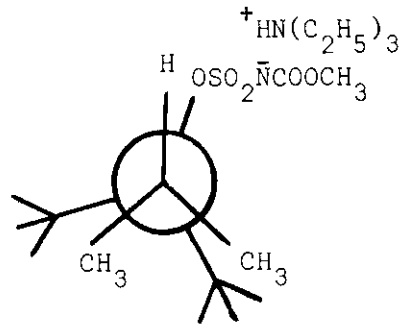
H	τ	Mult.
A	5.10,5.18	m
B	8.97	d
C	8.08	m
D	8.20	d
E	9.03	s
F	9.08	s

The molecular ion for XXII was of such weak intensity that no exact mass could be determined, but the fragmentation pattern was very indicative of the proposed structure. The following fragments and relative intensities were observed: $C_8H_{15}^+$ (100), $C_7H_{13}^+$(95), $C_5H_8^+$ (90), C_4H_9(85), C_3H_7 (65), C_3H_5 (83).

The absence of the other possible isomers of XXII is probably due to the preferred staggered conformation of the sulfamate ester in which the β-hydrogen lies between the two *t*-butyl groups and the large sulfamate ester function is as far as possible from the *t*-butyl groups (LVII).



LVII

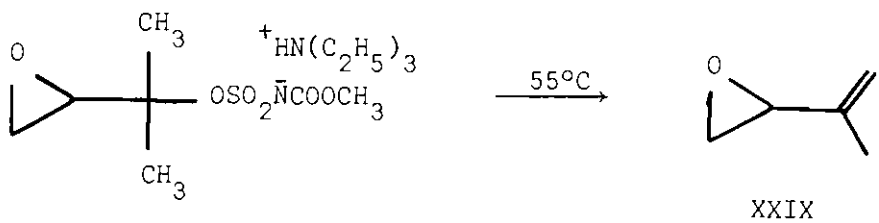


LVIII

In light of the proposed mechanism in which the departing anion also acts as the base in removing a proton, conformation LVII cannot undergo elimination to give a tetrasubstituted double-bond. In order to bring the β-hydrogen into range of the leaving group, both methyl and *t*-butyl groups must be eclipsed (LVIII), a very unfavorable conformation (33). With the only β-hydrogen unavailable for eliminating, the molecule reacts similar to the other neopentyl carbonium ions. As the tertiary carbonium ion develops the migration of a methyl from one of the *t*-butyl groups results in a second tertiary carbonium ion which subsequently deprotonates. Only methyls from *t*-butyl groups should be involved in migration since migration of a methyl from the isopropyl group would result in a less stable secondary carbonium ion.

The effect of the reaction conditions on other sensitive functional groups in a substrate was demonstrated by the dehydration of 3,4-epoxy-2-methyl-2-butanol (XXVIII). Treatment of XXVIII with XVII in a neat reaction at 55°C afforded 3,4-epoxy-2-methyl-1-butene (XXIX)

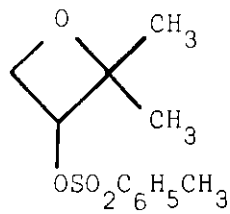
as the only product. XXIX was identified by its nmr and mass spectral data. The nmr showed absorptions for two vinyl protons [multiplets (1H) each at τ 4.83 and 5.00], one O-methine proton [multiplet at τ 6.65], two O-methylene protons [multiplet 2H at τ 7.25], and one vinyl methyl group [doublet at τ 8.37]. The theoretical exact mass is 84.119 as compared to the experimentally determined value of 84.120.



XXIX

This reaction contrasts sharply with the solvolysis of the corresponding tosylate (45) which is 80 per cent aqueous acetone undergoes rearrangement to form 2,2-dimethyl-3-p-toluenesulfonyl-oxetane (LXVIII) presumably *via* the 2,2-dimethyl-1-oxabicyclobutonium cation (LXIX). Similarly, 3-chloropropylene oxide when solvolyzed in glacial acetic acid results in a mixture of products including 3-acetoxy-oxetane (44). The rearrangement reportedly involves neighboring group participation of the oxirane oxygen at the developing positive charge on the α-carbon.

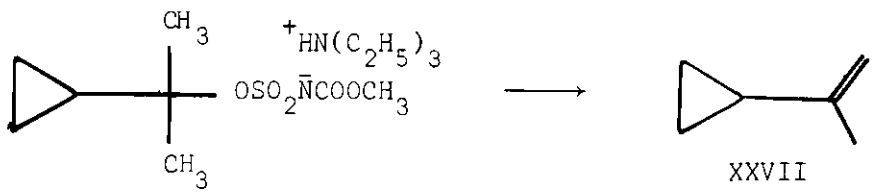
LXIX



LXVIII

The only product from the sulfamate ester solvolysis is the olefin XXIX. Apparently in this case no appreciable positive charge develops at the α-carbon prior to β-proton removal by the departing anion.

When dimethylcyclopropyl carbinol (XXVI) was treated with neat XVII, the only product was 2-cyclopropyl-propene (XXVII). Compound

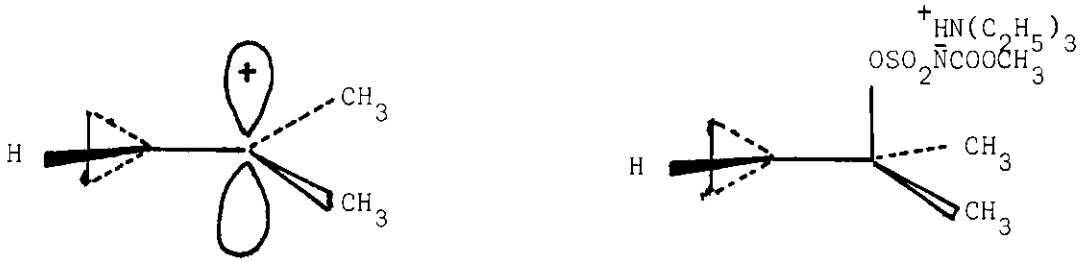


XXVII

XXVII was identified by its nmr and mass spectral data. The nmr spectrum showed absorptions for two vinyl protons [multiplet at τ 5.33], one vinyl methyl group [doublet (3H) at τ 8.36], one methine proton [complex triplet at τ 8.90], and two equivalent cyclopropyl methylenes [multiplet (4H) at τ 9.43]. The theoretical exact mass is 82.147 as compared to the experimentally determined value of 82.144.

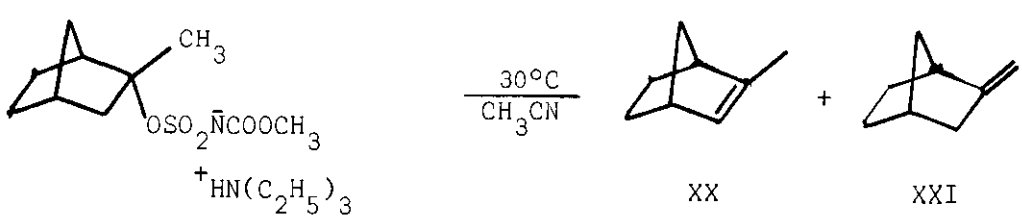
No cyclopropyl carbinyl rearrangement products were observed. The reason for the unidirectional pathway of the reaction is the conformational preference of the cyclopropyl carbinyl carbonium ion (34). The preferred conformation is that in which the cyclopropyl ring lies in a plane parallel to the axis of the vacant p-orbital. The

cyclopropyl ring lies *cis* to one methyl group and *trans* to the other.



In this orientation the maximum overlap of the β-carbon-carbon bond of the cyclopropyl ring and the vacant p-orbital is achieved. Significantly, it is this conformation in the developing carbonium ion which places the β-hydrogen of the cyclopropyl ring in an orthogonal relationship to the leaving sulfamate ester function. Since the hydrogen having the necessary *cis*-stereochemistry is unavailable to the departing anion for removal, one of the hydrogens from either methyl group is lost and XXVII is formed.

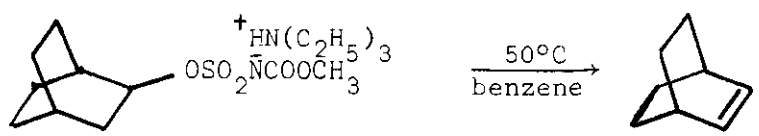
Compound XVII reacted with *endo*-2-methyl-[2.2.1]-bicyclo-2-heptanol (XVIII) in acetonitrile at room temperature to give an adduct which was thermolyzed in acetonitrile at 30°C to give 2-methyl-[2.2.1]-bicyclo-2-heptene (XX) and 2-methylene-[2.2.1]-bicycloheptane (XXI) in a 1:1 ratio.



These isomers were separated by glc using a 20 per cent carbowax column; XX had the shorter retention time. The nmr spectra are consistent with those reported for XX and XXI in the literature (18,19).

Of interest is the observation that no 1-methyl compounds were formed in the reaction. This fact indicates very rapid proton transfer to the leaving group while positive character is being developed at carbon-2. If such were not the case, the development of significant charge at carbon-2 before loss of a proton should result in products from Meerwein rearrangements (35). The ratio of XX:XXI (1:1) (glc) is slightly unusual since there are more methyl hydrogens than *cis*-ring hydrogens and the *exo*-methylene is the least strained double-bond. However, the one *cis*-β-ring hydrogen is in a fixed geometry with respect to the departing anion.

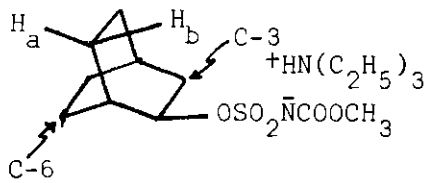
When XVII was reacted with [2.2.2.]-bicyclo-octanol (XXXVII) in benzene solution and subsequently heated to 60°C only one product, [2.2.2.]-bicyclo-2-octene (XXXVIII), was formed (20).



XXXVIII

This result was unexpected since the acetolysis of [2.2.2.]-bicyclo-2-octyl tosylate (36) gave over 70 per cent rearranged [3.2.1]-bicyclo-2-octyl acetate. Similar results were obtained from ethanolysis and hydrolysis reactions (36). These results indicate that the solvolysis involves the non-classical cation, LIX (37).

LIX

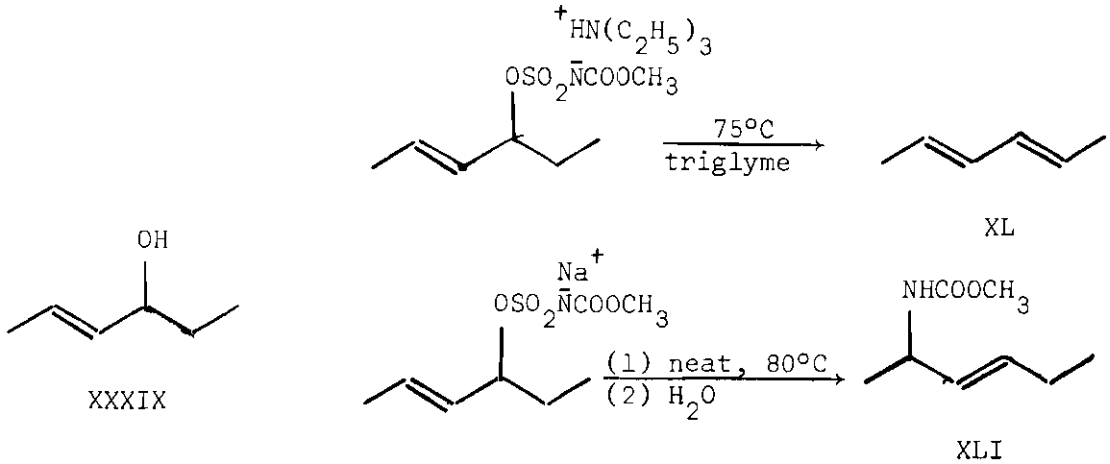


LX

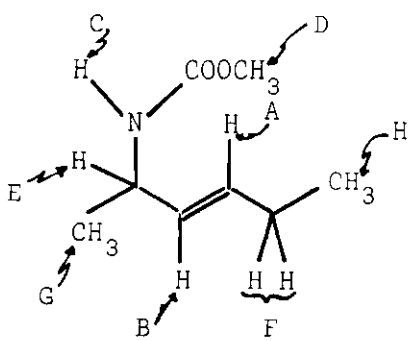
If the development of the non-classical ion is considered as an elimination reaction in which a proton (Ha or Hb) is removed and the methylene carbon (C-6) is the leaving group (see LX), then a polar solvent would be expected to favor a *trans*-elimination (loss of Hb) and a non-polar solvent would be expected to favor a *cis*-elimination (loss of Ha) (4). In benzene solution the Ha proton should be removed with subsequent development of the non-classical ion, followed by loss of the sulfamate ester function, and formation of rearranged products. This does not occur.

The conformation of the tight ion-pair appears to be the determining factor in this reaction. Apparently in the non-polar medium, since Ha is unavailable to the departing sulfamate anion, a proton is removed from the C-3 methylene with resultant formation of XXXVIII with no concurrent rearrangement.

In another example the reaction was applied to 4-hexen-3-ol (XXXIX). When XXXIX was added to XVII in triglyme solution and heated to 75°C, the only product obtained was 2,4-hexadiene (XL), identical to an authentic sample. If the sulfamate sodium salt were prepared and heated neat at 80°C, no olefin was obtained, but aqueous work-up led to isolation of the rearranged urethane, methyl N-2-hex-3-enylcarbamate (XLI) in high yield.



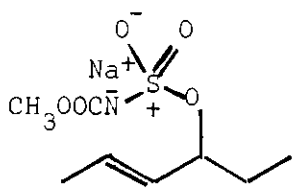
The structure of XLI was established by nmr and infrared spectra and exact mass determination. The infrared spectrum showed absorptions for N-H stretching at 3440 cm^{-1}, for C=O stretching in urethanes at 1720 cm^{-1}, and for disubstituted C=C at 1675 cm^{-1}. The theoretical exact mass is 157.125 as compared to the experimentally determined value of 157.127.



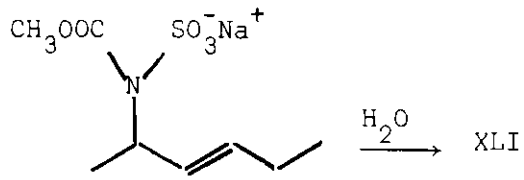
H	τ	Mult.
A,B	4.45	m
C	5.90	bs
D	6.40	s
E	8.00	m
F	8.35	m
G,H	8.95	m

The olefin formation observed with the triethylammonium salt was not obtained after exchanging the triethylammonium cation for a sodium cation. The crystalline sodium salt may have a solid state structure

which favors attack of the nitrogen on the carbon-carbon double-bond (LXI). This type of rearrangement (Sni') has precedent in allylic chlorosulfite rearrangements (38). In the sodium sulfamate ester case, attack of the nitrogen at the carbon-carbon double-bond probably results in the sodium sulfite salt (LXII) which is hydrolyzed in work-up to XLI. An intermediate of type XLII has been proposed in N,N-dialkyl-sulfamate ester thermolyses (10). The possibility of a concerted reaction with loss of sulfur trioxide and formation of the sodium salt of XLI cannot be ruled out. Under the reaction conditions it was difficult to determine if sulfur trioxide was evolved.



LXI



LXII

The conditions necessary to cause thermolytic decomposition of primary alkyl N-carbomethoxysulfamate esters were more vigorous than for secondary and tertiary cases. This is an expected result since partial formation of primary carbonium ions is energetically less favorable than partial formation of secondary or tertiary ones.

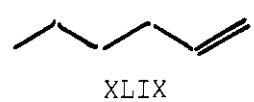
When 1-hexanol (XLVII) was reacted neat with XVII, and then heated to 95°C, the only product was methyl N-1-hexylcarbamate (XLVIII) which was obtained after a water work-up. The nmr spectrum and glc retention time of XLVIII and an authentic sample were identical.

$$CH_3(CH_2)_4CH_2OSO_2\bar{N}COOCH_3\ {}^{+}HN(C_2H_5)_3 \xrightarrow[2)\ H_2O]{1)\ \text{neat, } 95^\circ C} CH_3(CH_2)_4CH_2NHCOOCH_3$$

XLVIII

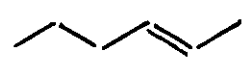
A completely different result was obtained if the triethylammonium gegenion was exchanged for a proton. This was easily accomplished by washing a benzene solution of the triethylammonium salt with a cold 2 per cent aqueous solution of hydrochloric acid. The neat free base (LXVIII) when heated to 150°C resulted in the distillation of a 1:1 ratio (glc) of 1- and 2-hexenes (XLIX and L) which were identical to authentic samples.

$$CH_3(CH_2)_4CH_2OSO_2NHCOOCH_3 \xrightarrow[\text{neat}]{150^\circ C}$$



XLIX

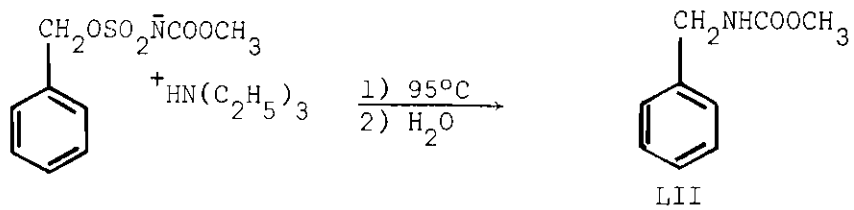
+



L

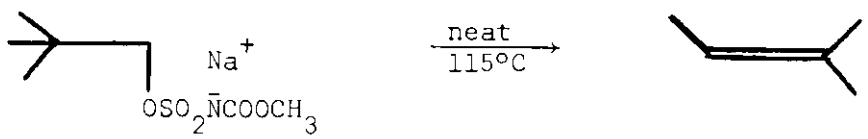
The explanation offered for these contrasting results is the possibility that olefin formation in this case is an auto-catalyzed reaction which occurs in the presence of the very acidic carbomethoxysulfamoyl proton. The acidic nature of the reaction medium is demonstrated by the apparent isomerization of 1-hexene to 2-hexene.

Another primary alcohol which resulted in urethane formation was benzyl alcohol (LI). When LI and XVII were reacted neat and heated to 95°C, aqueous work-up afforded methyl N-benzylcarbamate (LII) which was identical with an authentic sample.



LII

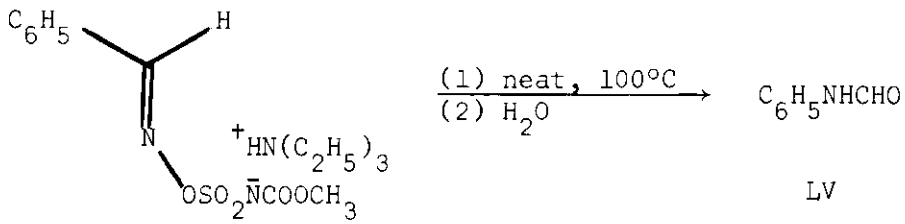
In another example 2,2-dimethyl-1-propanol (LIII) was the substrate. When LIII and XVII were reacted in benzene solution, converted to the neat sodium salt of the sulfamate ester, and then heated to 110°C, the only product was 2-methyl-2-butene (XXIV).



XXIV

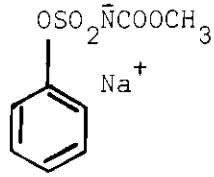
The urethane formation is probably an Sn2 reaction. An Sni mechanism similar to that proposed for N,N-dialkylsulfamate esters (10) is unlikely since in the case of 2,2-dimethyl-1-propanol (LIII), only 2-methyl-2-butene (XXIV) was formed. If a significant amount of charge developed at the α-carbon, then migration of a methyl group should have occurred to yield a *t*-amyl carbonium ion which on deprotonation would yield XXIV and 2-methyl-1-butene (XXV). The Sn2 pathway is indicated by the facts that lower temperatures (95°C) are required for urethane formation in the cases of 1-hexanol (XLVII) and benzyl alcohol (LI), and only when serious hindrance to backside attack, e.g., the *t*-butyl group in LIII, is present or at very high temperatures (150°C) does olefin formation occur.

Reaction of XVII neat with *syn*-benzaldehyde oxime (LIV) and subsequent heating to 100°C resulted in a Beckmann rearrangement with the formation of formanilide (LV) which was identical with an authentic sample.



Although the conditions of the Beckmann rearrangement generally result in complete dehydration of aldoximes to give the corresponding nitriles (29), no benzonitrile was observed in this reaction. The first-order Beckmann rearrangement is stereospecific with the group *trans* to the oxime-oxygen migrating to nitrogen. In the case of *syn*-benzaldehyde oxime the product expected from such a migration is the one observed. Although the possibility of a six-centered transition-state resulting in a *cis*-elimination exists, the absence of benzonitrile rules out this reaction pathway.

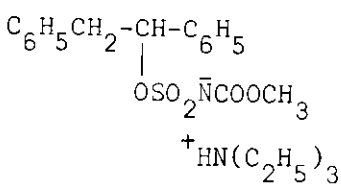
Having observed the nucleophilicity of the sulfamate ester nitrogen in reactions of primary alcohols, it was of interest to react XVII with phenol (XXX). Adding XXX neat to XVII resulted in a vigorous exothermic reaction after which the temperature was slowly raised to 200°C. No distillation occurred even at reduced pressures and aqueous work-up produced only starting material. Apparently triethylammonium phenyl-N-carbomethoxysulfamate is thermally very stable. Exchanging the gegenion for a sodium cation and carrying out the thermolysis yielded the same results.



$\xrightarrow[200°C]{\text{neat}}$ no reaction

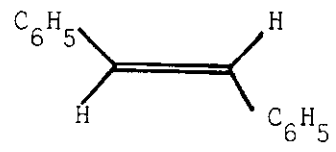
The thermolyses of the sulfamate esters of 3-*t*-butyl-2,2,4-trimethyl-2-pentanol (XIX), dimethylcyclopropyl carbinol (XXVI), 2-methyl-[2.2.1]-bicyclo-2-heptanol (XVIII), and [2.2.2.]-bicyclo-2-octanol (XXXVII) are indicative that the geometry of the hydrogen eventually lost to the leaving group is a critical factor in the product determination of these solvolyses. These cases indicated a *cis*-stereospecific elimination as the reaction pathway. To determine the *cis*-nature and the stereospecificity of the elimination the substrates 1,2-diphenylethanol (XLII), *erythro* (XLIV)- and *threo* (XLVI)-2-deuterio-1,2-diphenylethanol (10) were employed.

XLII when treated with XVII in benzene and heated to 50°C gave only *trans*-stilbene (XLIII) which was identical with an authentic sample.



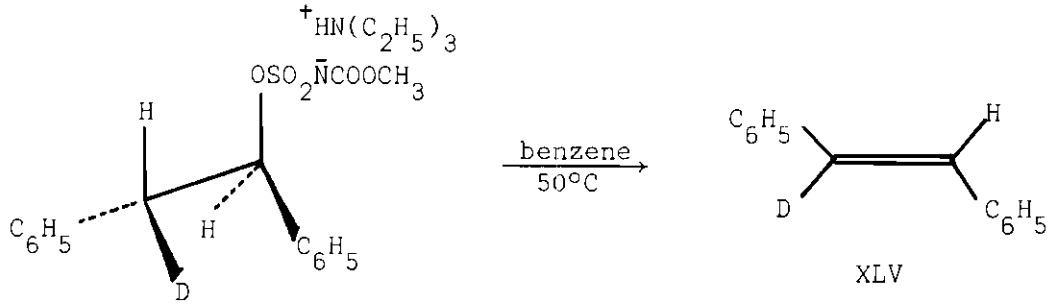
XIII

$\xrightarrow[50°C]{\text{benzene}}$



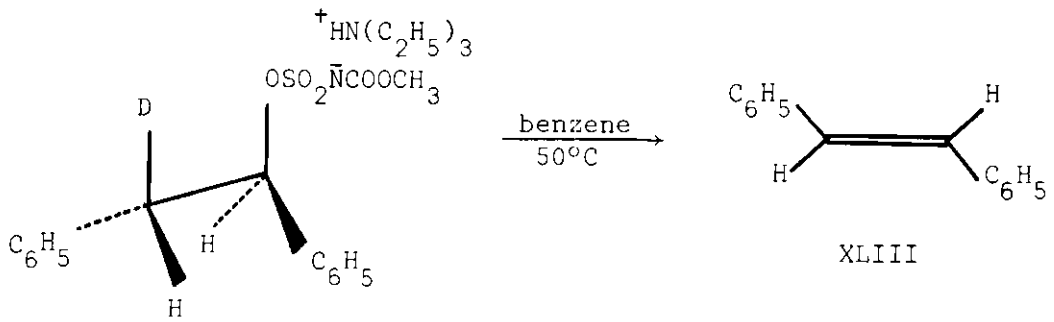
XLIII

When XLIV was reacted under similar conditions the only product obtained was α-deuterio-*trans*-stilbene (XLV) which was demonstrated by mass spectral analysis to contain a minimum of 0.97 deuterium atoms per molecule.



XIV XLV

When XLVI was treated under similar conditions, again only one product was formed, pure *trans*-stilbene (XLIII).



XV XLIII

These results clearly indicate a *cis*-stereospecific elimination. To be sure that the results of the reactions had not been predetermined by the use of the non-polar solvent benzene, the reactions were rerun exactly as before but changing the solvent to N,N-dimethylformamide. Even in going to the very polar solvent the resulting compounds and yields were invariant. The reaction remained a *cis*-stereospecific elimination even under conditions which strongly favored a *trans* reaction.

The *cis*-elimination is rationalized by removal of the β-proton by the departing anion which must remain on the same surface of the carbonium ion until it has removed a proton from an adjacent carbon. On the other hand, *trans*-eliminations require attack by the solvent from an antiparallel position. Alternation of the solvolysis mechanism from *cis* to *trans* can be correlated with the basicities of the solvents. The less basic solvents favor *cis*- and the more basic solvents favor *trans*-elimination. If a *trans*-elimination pathway were an alternative in this reaction, it should have occurred in the N,N-dimethylformamide solvolysis.

A kinetic study of the thermolyses of XIII, XIV, and XV was carried out in 95 per cent ethanol by measuring the appearance of silbene absorption in the ultraviolet spectral region as a function of time.

First-order rate constants were determined by plotting the logarithm of the ratio initial concentration of sulfamate ester: instantaneous concentration of sulfamate ester. The slopes of those straight lines are equal to (2.303)k since

$$\log \frac{C_o}{C} = 2.303\ kt$$

where C_o is the initial concentration of reactant (moles/liter), C is the instantaneous concentration of reactant (moles/liter), t is the time (seconds), and k is the first-order rate constant ($seconds^{-1}$) (see Figures 1-5). For XIII the activation parameters, energy of activation (Ea), enthalpy of activation ($\Delta H^{\ddagger}$), Gibbs free-energy of activation ($\Delta G^{\ddagger}$), and the entropy of activation ($\Delta S^{\ddagger}$), were determined

using solutions of three different concentrations (4.00×10^{-5} M, 3.00×10^{-5}M, and 2.00×10^{-5}M) and three different thermolytic temperatures (35°C, 46°C, and 52°C). Ea was obtained from the slope of a plot of log k vs. 1/T. Since

$$\log k = -\frac{Ea}{2.303\ RT}$$

where k is the first-order rate constant ($seconds^{-1}$), R is the gas constant (1.987 calories $°K^{-1}$ $mole^{-1}$) and T is the temperature (°K), the slope is equal to -Ea/2.303 R. $\Delta H^{\ddagger}$ is calculated from the relationship $Ea = \Delta H^{\ddagger} + RT$. $\Delta G^{\ddagger}$ is obtained from a plot of log k/T vs. 1/T since

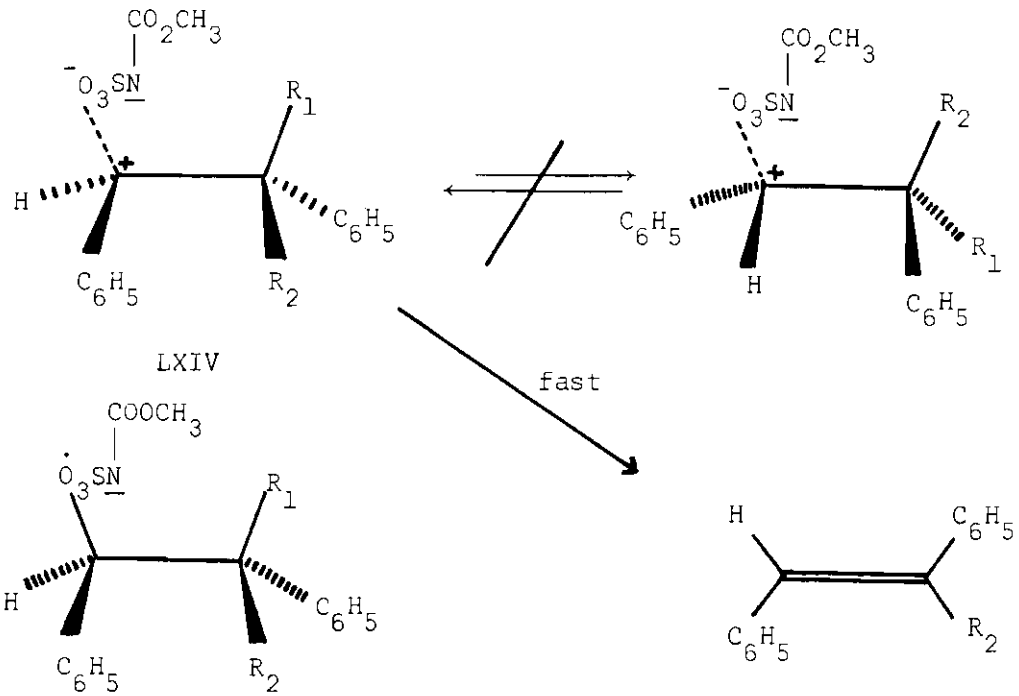
$$\log (k/T) = -\frac{\Delta G^{\ddagger}}{2.303\ RT}$$

the slope is equal to $-\Delta G^{\ddagger}/2.303$ R. $\Delta S^{\ddagger}$ is calculated from the relationship $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ (39). (See Figures 6 and 7 and Tables 2 and 3.)

The β-deuterium isotope effect determined from this data had a value $k_H/k_D = 1.05 \pm .02$ and $1.08 \pm .03$ for the *erythro-* and *threo-* isomers, respectively, at 35°C.

The product analysis from the thermolysis of XIII, XIV, and XV, the first-order kinetics of the reaction, the activation parameters, and the isotope effect date are consistent with a mechanism with an initial rate-limiting formation of an ion-pair followed by a fast

cis-β-proton transfer to the departing anion at a rate greater than the interconversion of the *erythro*- and *threo*-derived ion pairs (LXIVa, LXIVb).



a, R_1 = H, R_2 = D

b, R_1 = D, R_2 = H

Whether the proton is transferrred to nitrogen or oxygen in the ceparting anion is unclear. From a statistical and thermodynamic (based on bond energies (40)) viewpoint, the transition-state forming an O-H bond is energetically more favorable.

Although the thermolyses of XIII, XIV, and XV do not represent the mechanism for all the examples investigated, they do provide a basis upon which the other results may be rationalized.

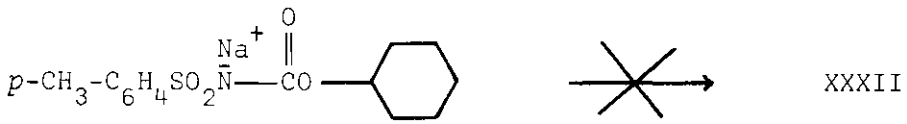
Table 2. Thermolyses of XIII, XIV, and XV in 95 Per Cent Aqueous Ethanol

Compound	Temp. (°C)	Conc.$\times 10^5$ (moles/liter)	$k \times 10^6$ (sec^{-1})
XIII	52	4.00	16.9
XIII	52	3.00	15.5
XIII	52	2.00	16.4
XIII	46	4.00	9.13
XIII	46	3.00	9.05
XIII	46	2.00	9.20
XIII	35	4.00	2.65
XIII	35	3.00	2.63
XIII	35	2.00	2.71
XIV	35	4.00	2.57
XIV	35	2.00	2.51
XV	35	4.00	2.43
XV	35	2.00	2.49

Table 3. Activation Parameters for Thermolysis of XIII in 95 Per Cent Aqueous Ethanol

E_a (kcal/mole)	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta G^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)
+22.4 ± 0.5	+21.7 ± 0.5	+22.8 ± 0.5	-3.3 ± 0.9

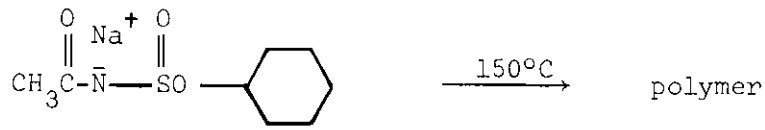
It was of interest to determine how other systems might compare as leaving groups in reactions similar to the thermolytic decomposition of alkyl N-carbomethoxysulfamate esters. The adduct formed from cyclohexanol and *p*-toluenesulfonyl isocyanate was pyrolyzed as its sodium salt (LXIII). No olefin was formed.



LXIII 100°C XXXII

The fact that this system does undergo a similar elimination to the alkyl N-carbomethoxysulfamate esters, although at higher temperatures, in poorer yields, and only with tertiary alcohols, has recently been demonstrated (12).

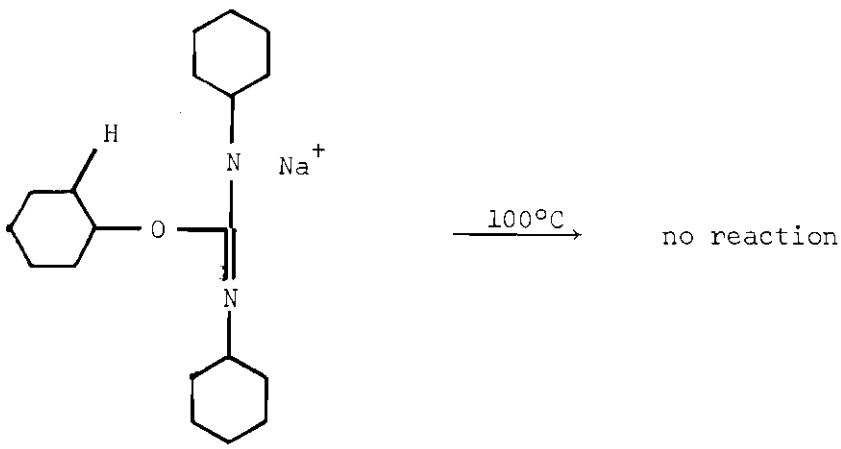
Similarly, an N-sulfinyl acetamide adduct was investigated. N-sulfiryl acetamide was treated with cyclohexanol and sodium hydride and the resulting sodium salt (LXV) was pyrolized at 150°C resulting only in polymerization.



LXV polymer

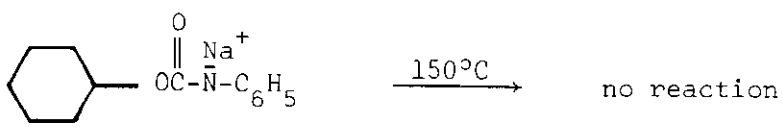
Another example was the adduct formed from dicyclohexylcarbodiimide and sodium cyclohexyl alkoxide. Treatment of sodium cyclohexyl alkoxide with dicyclohexylcarbodiimide in tetrahydrofuran followed by removal of solvent produced a clear yellow oil, presumably LXVI, which

underwent no change on heating at 100°C for 6 hours.



LXVI

Similarly, the adduct of sodium cyclohexyl alkoxide and phenyl isocyanate was investigated. Pyrolysis of this adduct (LXVII) at 150°C failed to produce any cyclohexene.



LXVII

In all of the above cases a similar spacial arrangement exists for the leaving group relative to a β-proton as in the sulfamate ester case. The important difference is, with the exception of the *p*-totuene-sulfonyl isocyanate adduct, that all of the departing anions in these reactions are strong bases and hence poor leaving groups.

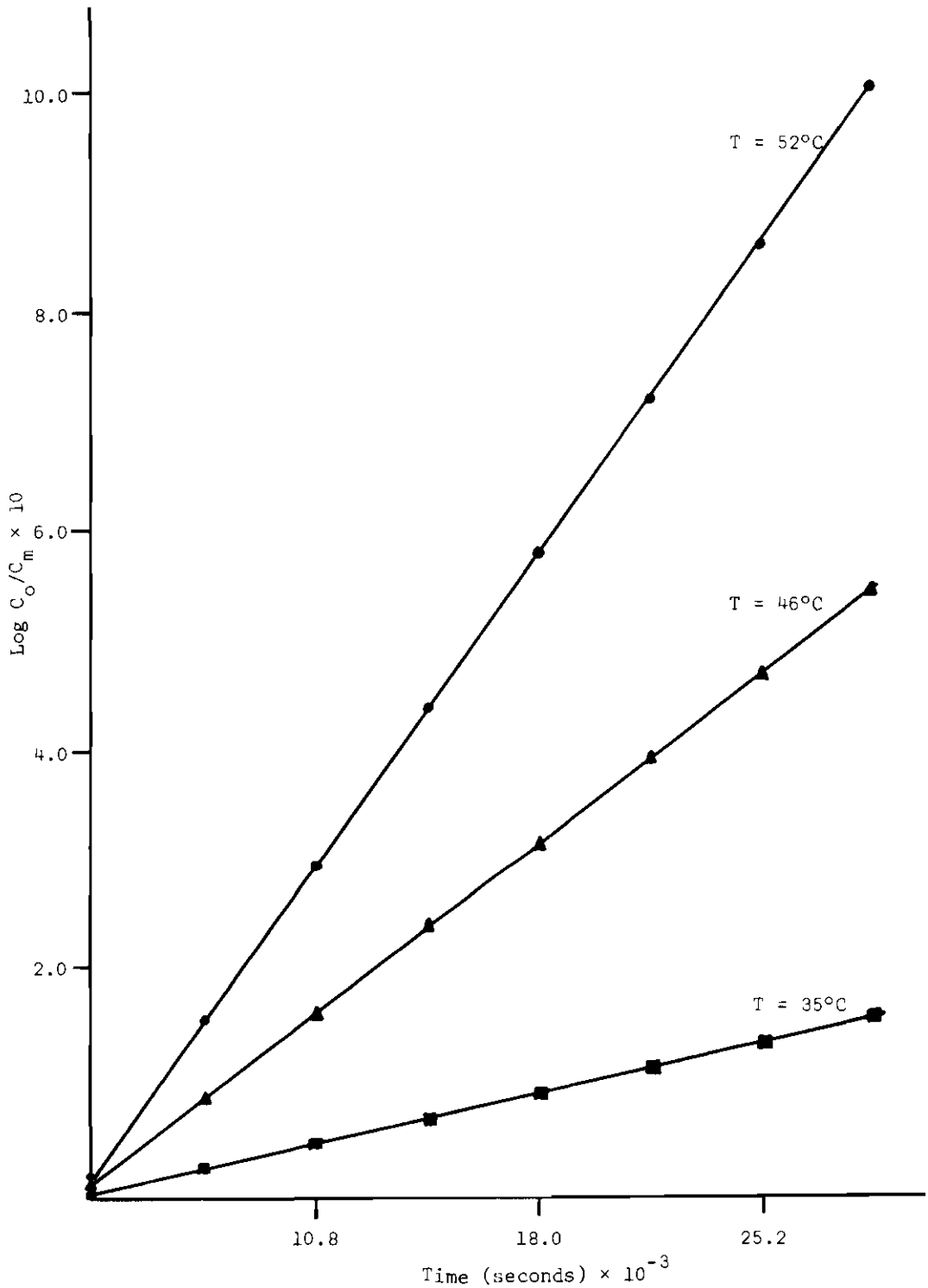


Figure 1. Thermolysis of XIII (4.00×10^{-5}M)
(•, 52°C; Δ, 46°C; □, 35°C)

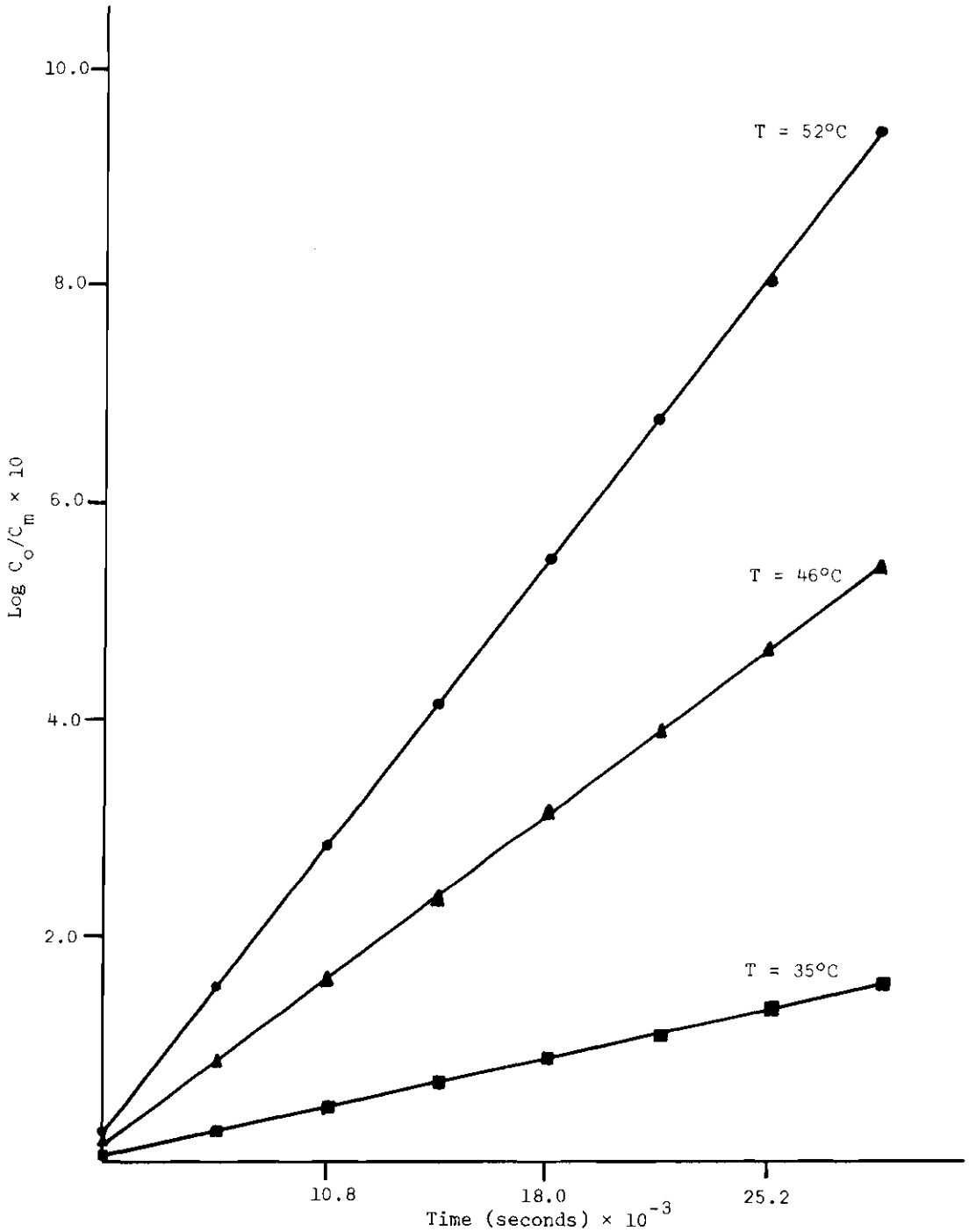


Figure 2. Thermolysis of XIII (3.00×10^{-5}M) (•, 52°C; Δ, 46°C; □, 35°C)

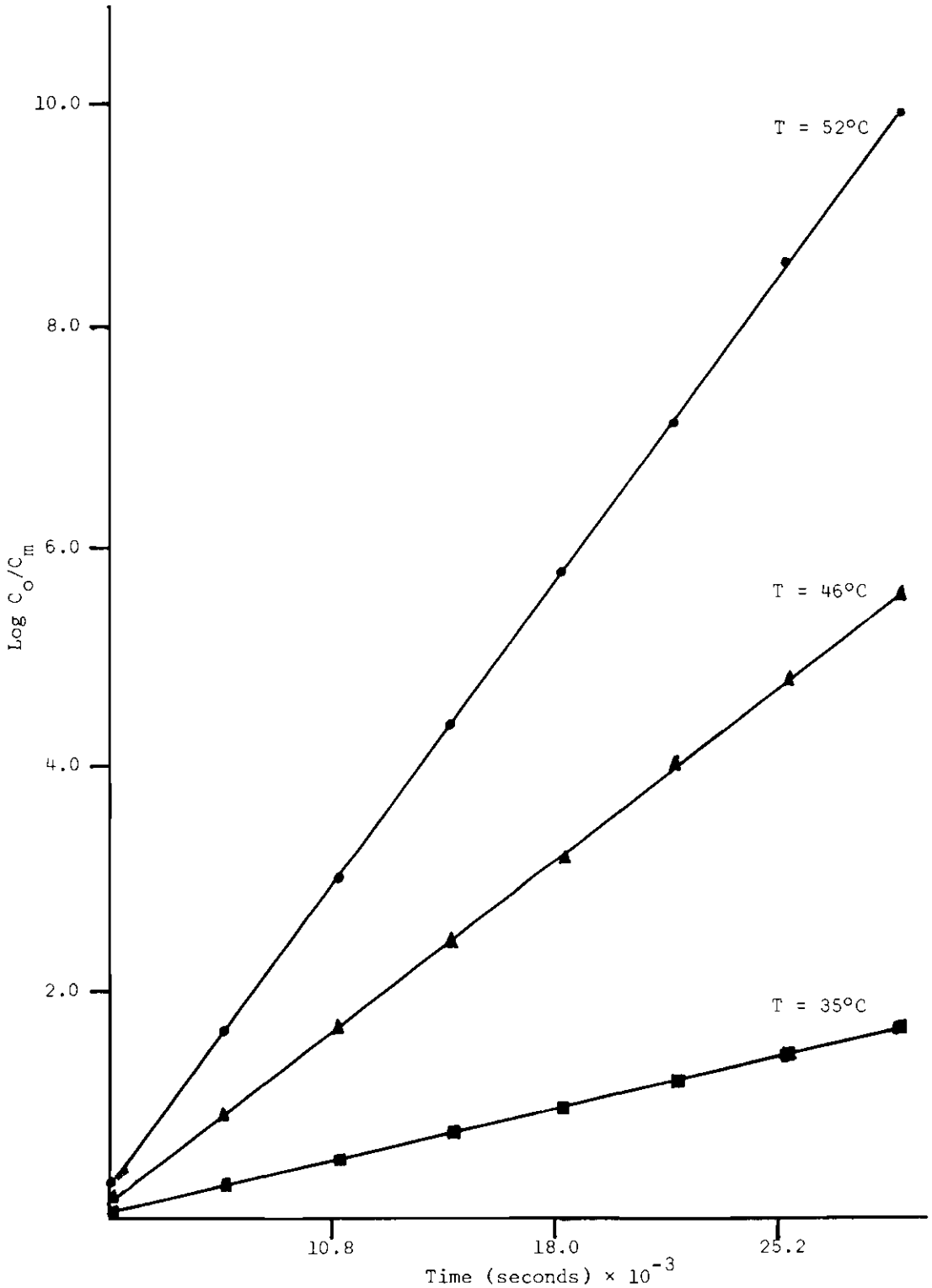


Figure 3. Thermolysis of XIII (2.00×10^{-5}M) (•, 52°C; Δ, 46°C; □, 35°C)

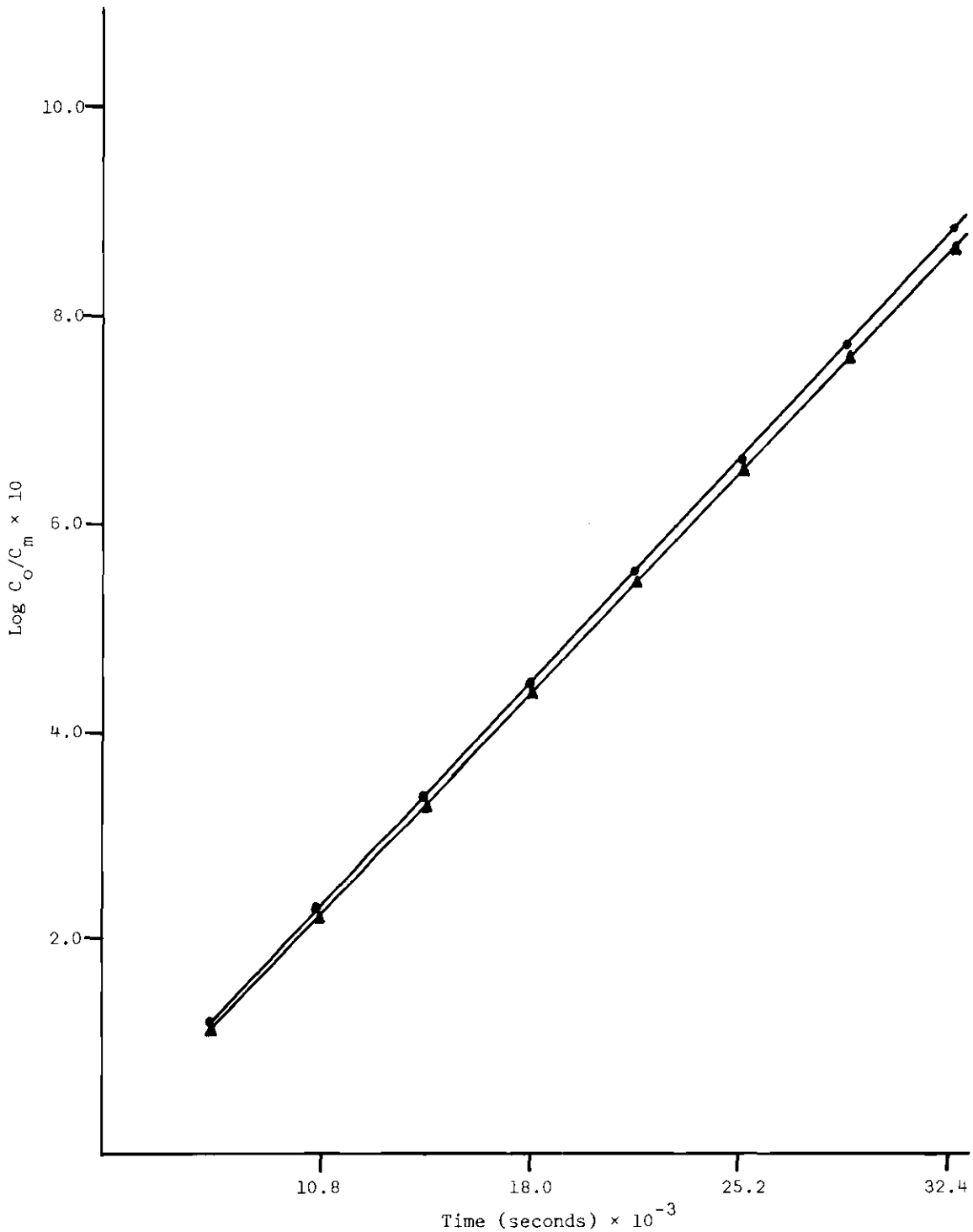


Figure 4. Thermolysis of XIV at 35°C
(•, 4.00 × 10^{-5}M; Δ, 2.00 × 10^{-5}M)

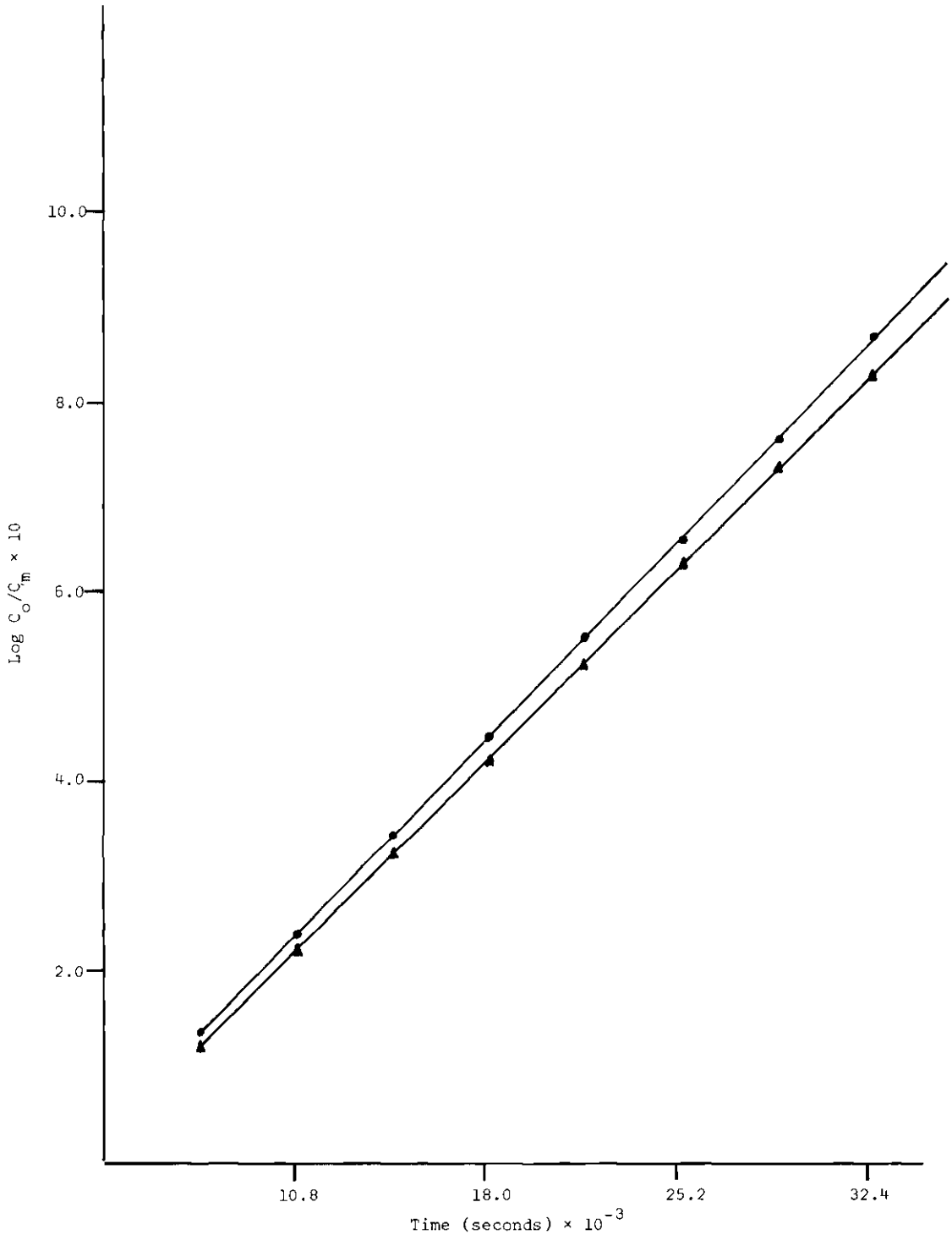


Figure 5. Thermolysis of XV at 35°C
(•, 4.00×10^{-5}M; Δ, 2.00×10^{-5}M)

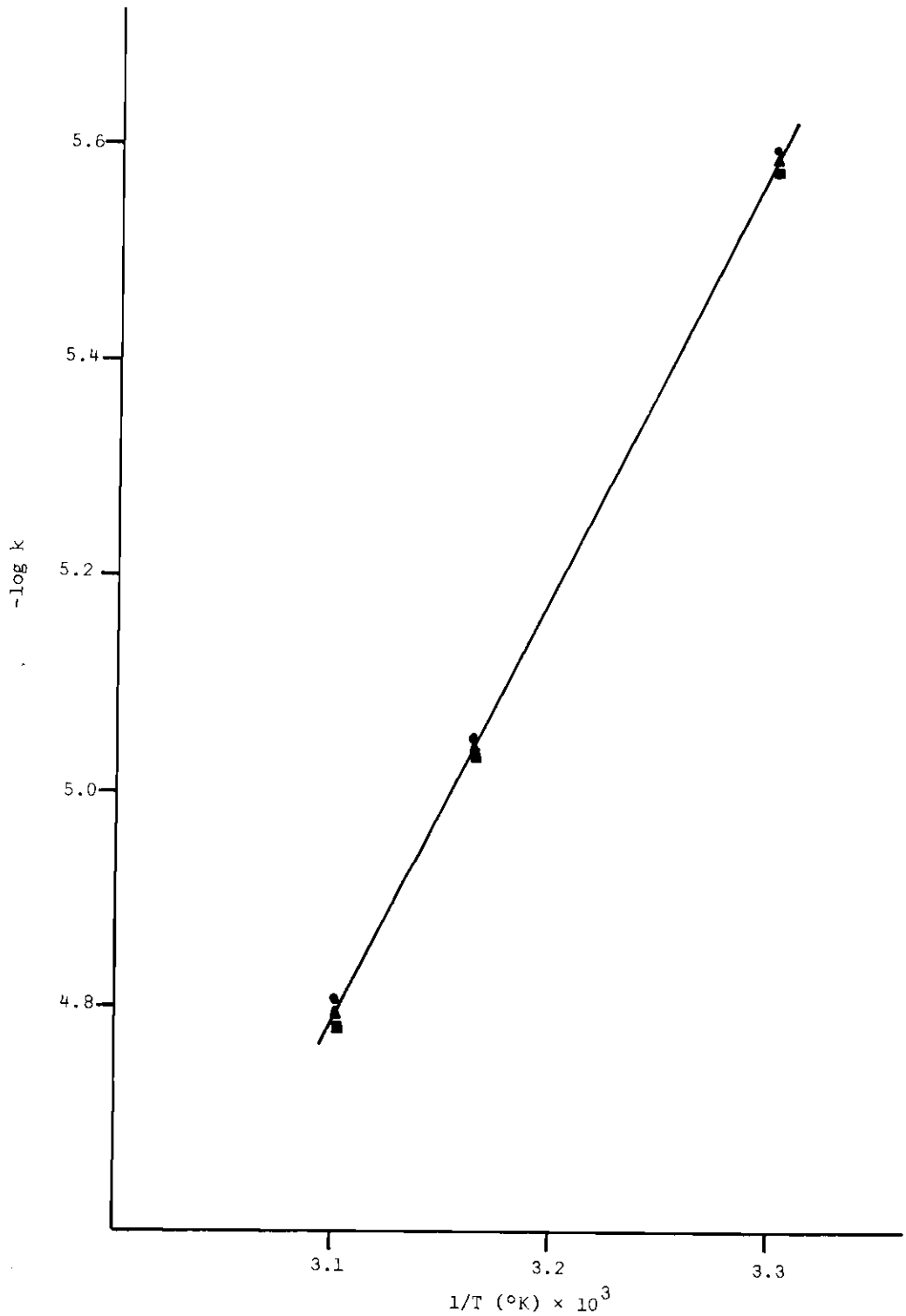


Figure 6. Determination of Ea. Plot of -Log k vs. 1/T
(•, 4.00 × 10^{-5}M; Δ, 3.00 × 10^{-5}M; □, 2.00 × 10^{-5}M)

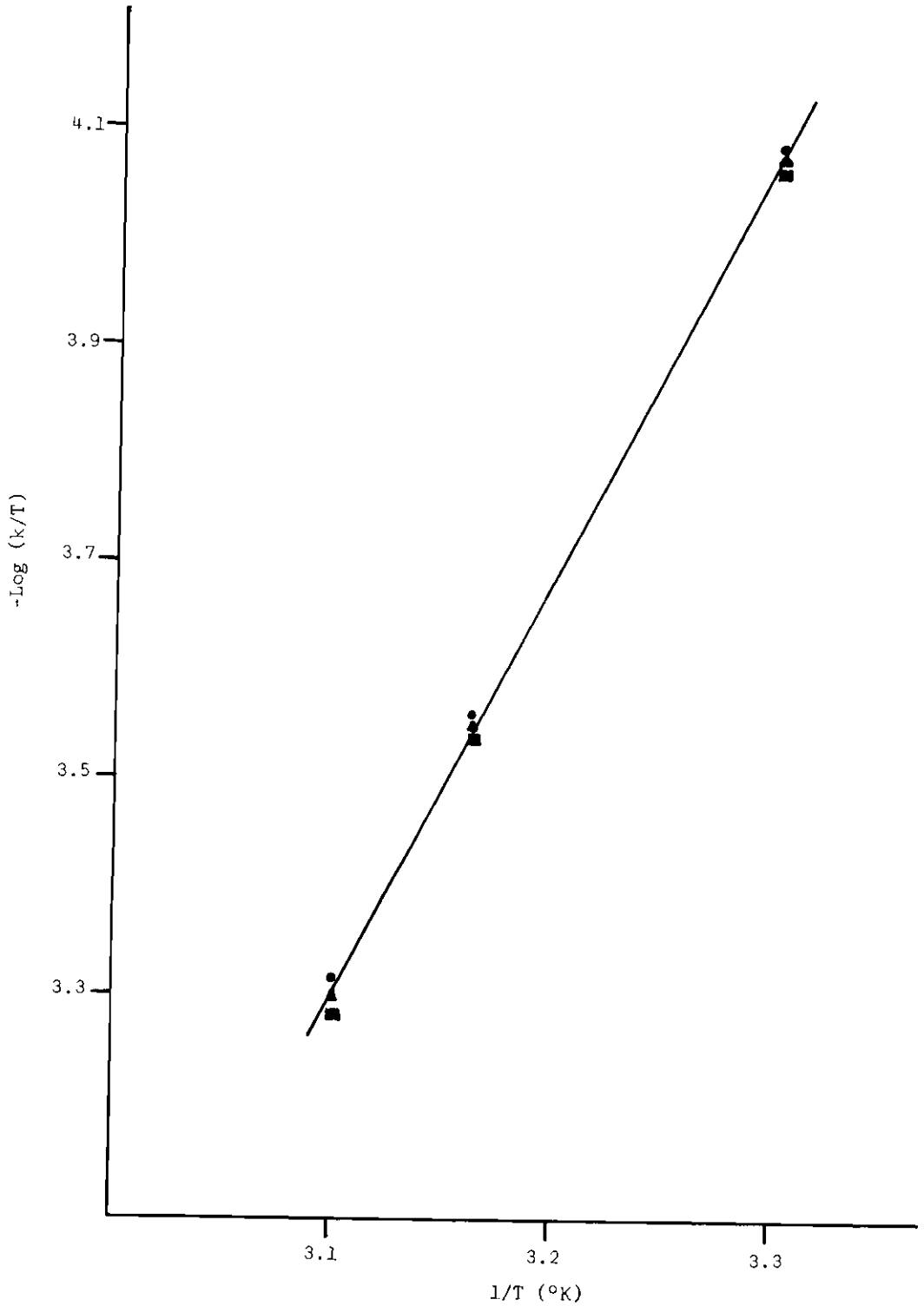


Figure 7. Determination of $\Delta G^{\ddagger}$. Plot of -Log (k/T) vs. 1/T (•, 4.00×10^{-5}M; Δ, 3.00×10^{-5}M; □, 2.00×10^{-5}M)

CHAPTER IV

CONCLUSIONS

(Carboxysulfamoyl)triethylammonium hydroxide, inner salt, methyl ester (XVII) was synthesized and shown to react with a broad spectrum of alcohols resulting in alkyl N-carbomethoxysulfamate esters (IV). The scope and synthetic usefulness of the sulfamate ester function as a leaving group in thermolytic dehydration reactions was demonstrated by the facile conversion of tertiary and secondary alcohols to olefins and primary alcohols to urethanes.

The following are the results of the product analysis of these thermolyses (alcohol, products): cyclohexanol (XXXI), cyclohexene (XXXII); 3,3-dimethyl-2-butanol (XXXIII), 3,3-dimethyl-1-butene (XXXIV), 2,3-dimethyl-1-butene (XXXVI), 2,3-dimethyl-2-butene (XXXV); 2-methyl-[2.2.1.]-bicyclo-2-heptanol (XVIII), 2-methyl-[2.2.1.]-bicyclo-2-heptene (XX), 2-methylene-[2.2.1]-bicycloheptane (XXI); [2.2.2.]-bicyclo-2-octanol (XXXVII), [2.2.2.]-bicyclo octene (XXXVIII); 2-methyl-2-butanol (XXIII), 2-methyl-2-butene (XXIV), 2-methyl-1-butene (XXV); 3-*t*-butyl-2,2,4-trimethyl-3-pentanol (XIX), 3-*t*-butyl-2,3,4-trimethyl-1-pentene (XXII); 3,4-epoxy-2-methyl-2-butanol (XXVIII), 3,4-epoxy-2-methyl-1-butene (XXIX); dimethylcyclopropylcarbinol (XXVI), 2-cyclopropylpropene (XXVII); 4-hexen-3-ol (XXXIX), methyl N-2-hex-3-enylcarbamate (XLI), 2,4-hexadiene (XL); 1-hexanol (XLVII), 1-hexene (XLIX), 2-hexene (L), methyl N-hexylcarbamate (XLVIII); benzyl alcohol (LI), methyl

N-benzylcarbamate (LII); 2,2-dimethyl-1-propanol (LIII), 2-methyl-2-butene (XXIV); *syn*-benzaldehyde oxime (LIV), formanilide (LV); 1,2-diphenylethanol (XLII), *trans*-stilbene (XLIII); *erythro*-2-deuterio-1,2-diphenylethanol (XLIV), α-deuterio-*trans*-stilbene (XLV); *threo*-2-deuterio-1,2-diphenylethanol (XLVI), *trans*-stilbene (XLIII).

Stereochemically the reaction was established as a *cis*-stereospecific elimination by the formation of only protio-*trans*-stilbene (XLIII) from *threo*-2-deuterio-1,2-diphenylethyl-N-carbomethoxysulfamate triethylammonium salt (XV) and only α-deuterio-*trans*-stilbene (XLV) from the corresponding *erythro*-compound (XIV).

The first-order rate constants for XIII, XIV, and XV were determined spectrophotometrically ($k_{35°C}$ = 2.66×10^{-6}, 2.54×10^{-6}, and 2.46×10^{-6} sec^{-1}, respectively) and a small β-deuterium isotope effect was observed (k_H/k_D = 1.05 for *erythro*- and 1.08 for *threo*-compound). Activation parameters were calculated for the thermolysis of XIII: Ea = 22.4 kcal/mole, $\Delta H^{\ddagger}$ = 21.7 kcal/mole, $\Delta G^{\ddagger}$ = 22.8 kcal/mole, $\Delta S^{\ddagger}$ = -3.3 e.u.

These kinetic and stereochemical results are consistent with an initial rate-limiting formation of an ion-pair followed by a fast *cis*-β-proton transfer to the departing anion at a rate greater than the interconversion of *erythro*- and *threo*-ion-pairs.

Portions of this research have been previously reported (41,42) and the method has been applied to steroidal alcohols (43).

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*Abbreviations used herein follow the form employed by *Chemical Abstracts*, 55, IJ (1961).

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VITA

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