The Mechanism of Alkyl Migrations in Nitrogen ylids

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THE MECHANISM OF ALKYL MIGRATIONS IN NITROGEN YLIDS

BY

WESLEY J. BRUXVOORT

A thesis submitted in partial fulfillment of the requirements for the degree Master of Science, Major in Chemistry, South Dakota State University

1968

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THE MECHANISM OF ALKYL MIGRATIONS IN NITROGEN YLIDS

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser / Date

Head, Chemistry Department / Date
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INTRODUCTION

The purpose of this research is to study the mechanism of alkyl migration in nitrogen ylids.

There are several possible mechanisms by which the migration may take place.

A. The alkyl group, R, may migrate intermolecularly.

During the migration the R group would exist as a free carbonium ion separated from the parent molecule by solvent.

B. The alkyl group, R, may migrate cis by a concerted mechanism. The alkyl group remaining in the same plane during the migration. Isomers would not be expected because of the facile inversion about the nitrogen atoms.

C. The alkyl group, R, may migrate both cis and trans, through a concerted mechanism. The alkyl group migrating to either side of the nitrogen.
To study the mechanism of alkyl migration, triazolidium ylids (1) were used in which the alkyl migration may or may not produce ring enlargement. If only ring enlargement occurs, then the rearrangement must take place via mechanism (B.) or (C.). If, however, a large amount of polymeric product (2) and only a small amount of the ring enlarged product are obtained, then the rearrangement must proceed through mechanism (A.).
Stevens was first to report that certain quaternary ammonium salts will undergo smooth rearrangement with the migrating group going from nitrogen to carbon. In Stevens' initial observation, he found that phenacylbenzyldimethyl-ammonium bromide (3) rearranged under aqueous alkaline condition to give (1-benzoyl-2-phenyl) ethyl-dimethylamine (4).

\[
\begin{align*}
\text{C}_6\text{H}_5\text{COCH}_2^+\text{N}^+\text{CH}_2\text{C}_6\text{H}_5 & \xrightarrow{\text{OH}^-} \text{C}_6\text{H}_5\text{COCH}^-\text{N(CH}_3)_2 \quad (3) \\
\text{C}_6\text{H}_5\text{COCH}^-\text{N(CH}_3)_2 & \xrightarrow{\text{OH}^-} \text{C}_6\text{H}_5\text{COCH}^+\text{N}^+\text{CH}_2\text{C}_6\text{H}_5 \quad (4)
\end{align*}
\]

The observation that an electron-withdrawing substituent in the migrating group favored the rearrangement led Stevens to postulate that the rearrangement proceeded first by proton removal from the phenacyl group, followed by generation of the benzylcarbanion immonium intimate ion pair which collapses rapidly and internally (Scheme I).

Scheme I

\[
\begin{align*}
\text{C}_6\text{H}_5\text{COCH}_2^+\text{N}^+\text{CH}_2\text{C}_6\text{H}_5 & \xrightarrow{\text{OH}^-} \left[ \text{C}_6\text{H}_5\text{COCH}^-\text{N}^+\text{CH}_2\text{C}_6\text{H}_5, \text{CH}_3 \right] \\
\left[ \text{C}_6\text{H}_5\text{COCH}^-\text{N}^+\text{CH}_2\text{C}_6\text{H}_5, \text{CH}_3 \right] & \xrightarrow{\text{CH}_3} \left[ \text{C}_6\text{H}_5\text{COCH}^-\text{N}^+\text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5 \right] \\
\left[ \text{C}_6\text{H}_5\text{COCH}^-\text{N}^+\text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5 \right] & \xrightarrow{\text{CH}_3} \left[ \text{C}_6\text{H}_5\text{COCH}^-\text{N}^+\text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5 \right]
\end{align*}
\]
This mechanism was rejected when Campbell et al. showed that the Stevens rearrangement of optically active phenacyl dimethyl(1-phenylethyl)ammonium bromide (5) afforded optically active dimethyl(1-phenacyl-2-phenylpropyl)amine (6). Therefore the rearrangement must proceed through an intramolecular and concerted mechanism.

An intramolecular, concerted mechanism was also proposed for the Stevens rearrangement by Wittig et al. and Hauser and Kantor. They proposed that the rearrangement proceeded via the formation of an ammonium ylid, the carbanion of which attacked the migrating group. This mechanism would account for retention of configuration. In the case where the migrating group is benzyl, electron withdrawing groups substituted in the para position cause an increase in the rate of migration relative to hydrogen. This phenomenon is in accord with the postulated mechanism which pictures a nucleophilic attack by a carbanion on benzyl group.

More recently, 1960, Wawzonek and Yeakey have found that
dimethyl(p-nitrobenzyl)ammonium-N-acetylimine (7) will undergo a Stevens type rearrangement. In this case the migrating terminus is a nitrogen atom.

\[
\begin{align*}
\text{(7)} & \quad \text{(8)} \\
\begin{array}{c}
\text{CH}_3 \text{N}^+ \text{NCOCH}_3 \\
\text{CH}_2 \text{C}_6 \text{H}_4 \text{NO}_2
\end{array} & \quad \begin{array}{c}
\text{CH}_3 \text{N} = \text{C} = \text{O} \\
\text{CH}_2 \text{C}_6 \text{H}_4 \text{NO}_2
\end{array}
\end{align*}
\]

It has also been shown⁷ that if the groups are simple alkyl groups, other than benzyl or allyl, that the Stevens rearrangement does not occur. A N—N bond cleavage takes place to give an isocyanate and tertiary amine.

The mechanism of the aminimide rearrangement has recently been studied by Wadsworth.⁸ It is stated that the isocyanate formation can be assumed like the Curtius rearrangement to proceed by either a nitrene (a), or a concerted pathway (b). The cyclic aminimide (9) could be expected to undergo a Wawzonek type of rearrangement if the R group is benzyl or allyl. If the R group
is an alkyl group other than benzyl or allyl, and if the rearrangement is through a nitrene intermediate, then the cyclic aminimide (9) could be expected to undergo rearrangement to give an isocyanate. However, if the formation of isocyanate is through a concerted mechanism, the transition state would involve a high energy bicyclic intermediate (10). It is therefore doubtful that in this case the rearrangement would give an isocyanate.

To test this theory, cyclic aminimides were prepared. In the case of 1-benzyl-1,4-dimethyl-3-oxopyrazolidinium hydroxide inner salt (11), a Wawzonek type rearrangement took place to give
1,4-dimethyl-2-benzyl-3-pyrazolidinone (12). Pyrolysis of the cyclic aminimide (13) did not result in N—N cleavage to give an isocyanate as in the noncyclic case, but underwent ring opening to give 1,1-dimethyl-2-methacrylyl-hydrazine (14). The lack of isocyanate formation with this cyclic aminimide lends support for a concerted mechanism in the formation of isocyanate with noncyclic aminimides.

Cyclic hydrazonium ylids, which will undergo rearrangement via methyl migration, have been discovered. These ylids were prepared by means of an interesting phosphoramidate synthesis (Scheme II).

Scheme II

\[
\begin{align*}
2 (\text{CH}_3)_2\text{NNH}_2 + \text{CCl}_4 + (\text{C}_2\text{H}_5\text{O})_2\text{P} &\rightarrow (\text{C}_2\text{H}_5\text{O})_2\text{P}^+\text{H} - \text{NN}(\text{CH}_3)_2 + \text{CHCl}_3 \\
(15) &\quad (16) &\quad (17) &\quad + \\
(\text{C}_2\text{H}_5\text{O})_2\text{P}^-\text{NN}(\text{CH}_3)_2 &\rightarrow (\text{CH}_3)_2\text{N}^-\text{NH}_3 \text{Cl}^- \\
(19) &\quad (18)
\end{align*}
\]

\[
\begin{align*}
(\text{C}_2\text{H}_5\text{O})_2\text{P}^-\text{NN}(\text{CH}_3)_2 &\rightarrow \left[(\text{CH}_3)_2\text{N—N=C=O}\right] + (\text{C}_2\text{H}_5\text{O})_2\text{P}^- \\
(20) &\quad (21)
\end{align*}
\]

\[
\begin{align*}
(\text{CH}_3)_2\text{N}^+\text{N}^- &\rightarrow \text{O=C=O} \\
(\text{22}) &\quad (23)
\end{align*}
\]
phosphoramidate anion (19), prepared by reacting the amide (17) with sodium hydride, was reacted with carbon dioxide to give dimethyl aminoisocyanate (21). Dimethyl aminoisocyanate, which cannot be isolated, forms a dimer (23) upon standing or it can be trapped by adding another isocyanate to give a mixed dimer (22).

\[
\text{(23)} \quad \text{(24)}
\]

When the dimer (23) was heated for 15 minutes at 200° Centigrade it rearranged to give a triazole (24) in 96% yield. The ylid (23) showed carbonyl absorption in the infrared at 1790 and 1670 cm\(^{-1}\), upon pyrolysis the two peaks converged to give carbonyl absorption at 1730 with an overtone at 1780 cm\(^{-1}\).
EXPERIMENTAL

**Diethyl N-pentamethylenimine phosphoramidate.** To a standard taper 19/22, three neck, 500 milliliter flask was added diethyl phosphite (34 grams, 0.25 mole), carbon tetrachloride (38 grams, 0.25 mole), and 60 milliliters of dry xylene. The flask was placed in an ice bath and equipped with a thermometer, a 100 milliliter dropping funnel and a magnetic stirrer. N-Aminopiperidine (50.5 grams, 0.5 mole) was placed in the dropping funnel and added to the solution at a rate such that the temperature did not exceed 40°C Centigrade. After the addition was complete, the solution was cooled and stirred for an additional hour.

The solution was filtered, and 42 grams of N-aminopiperidine hydrochloride collected. The filtrate was evaporated at reduced pressure on a rotary evaporator. The residue was recrystallized three times from 300 milliliters of hot heptane. The product, consisting of white crystals melting at 72-73°C Centigrade, weighed 30 grams (61% of theoretical yield).

**4 n-Butyl-1-pentamethylene-5-one\(\Delta^2\)-1:2:4-3-oxotriazolidium hydroxide inner salt.** To a standard taper 19/22, three neck, 500 milliliter flask, equipped with a magnetic stirrer, was added dry benzene (300 milliliters) and 50% sodium hydride (6.12 grams, 0.127 mole). To this slurry, diethyl N-pentamethylenimine phosphoramidate (25 grams, 0.127 mole) was added slowly. These were allowed to react overnight. During this time, hydrogen was evolved.
The flask was placed in an ice bath and equipped with a thermometer, a calcium chloride tube, a magnetic stirrer, and a glass tube fitted through a rubber stopper. The glass tube was connected to a tank containing dry nitrogen and positioned with the end of the tube above the liquid. Then the flask was flushed with dry nitrogen. The glass tube was connected to a flask containing dry ice and, with the end of the tube placed below the surface of the liquid, carbon dioxide was slowly bubbled through the solution at such a rate that the temperature did not exceed 10° Centigrade. When the exothermic reaction was complete, the flask was allowed to come to room temperature and n-butyl isocyanate (12.8 grams, 0.127 mole) was added quickly. The flask was flushed again with dry nitrogen, sealed, and allowed to stand for one week. During this one week period, a semi-crystalline solid precipitate formed. The supernatant liquid was decanted, and the semi-solid material was extracted three times with 100 milliliter portions of warm benzene. The liquid fractions were combined and evaporated under reduced pressure on a rotary evaporator. The residue was recrystallized three times from 200 milliliter portions of carbon tetrachloride. The purified product, consisting of white platelets melting at 165-167° Centigrade, weighed 12.1 grams (35% of theoretical yield).

Anal. Calcd. for C_{11}H_{9}O_{2}N_{3}: C, 58.65; H, 8.51. Found: C, 57.75; H, 8.66. Molecular weight Calcd: 225.29, Found: 228.

Attempted rearrangement of 4 n-butyl-1-pentamethylene-5-one-Δ^2-1:2:4-3-oxotriazolidinium hydroxide inner salt. The
rearrangement of the ylid was attempted by heating it at various temperatures until the carbonyl peaks in its infrared spectrum at 1800 and 1680 cm\(^{-1}\) converged at 1710 cm\(^{-1}\). In one attempt 3.5 grams of the ylid was placed in a 50 milliliter, 19/22 standard taper flask. The flask was connected to a condenser to collect any vapors that were given off. The flask was heated at 170-180° Centigrade for seven hours. Attempts were made to isolate the product by recrystallization of the oil from various solvents, but the only crystals isolated were from xylene and identified as the starting material by comparing the infrared spectrum of the isolated crystals with that of the starting material. Attempts were also made to distill the heated material at reduced pressure but this failed due to the formation of polymeric material.

Other attempts were made to rearrange the ylid by heating it at higher temperatures, up to 210° Centigrade, but again no rearranged product could be isolated.

**Preparation of 1-nitroso-hexamethylenimine.** To a standard 24/40 three neck, three liter flask equipped with a magnetic stirrer, a thermometer, a heating mantle, and a 500 milliliter dropping funnel, was added practical grade hexamethylenimine (270 grams, 2.72 moles, produced by Eastman Kodak) and 78 milliliters of water. The solution was made slightly acidic, pH 5.5-6.5, by slowly adding 227 milliliters of concentrated hydrochloric acid from the dropping funnel. The solution was heated to 70° Centigrade and sodium nitrite (195 grams, 2.33 moles) in 285 milliliters of
water was added over a one hour period. The solution was kept at a temperature between 65 and 70° Centigrade for an additional two hours. At the end of this period the solution was cooled, and the yellow upper layer was removed by means of a separatory funnel. The aqueous layer was extracted with three 150 milliliter portions of ether. The upper layer and the ether layers were combined and dried over calcium chloride for eight hours. The ether was evaporated on a steam bath and the residue distilled under reduced pressure. The yield of 1-nitroso-hexamethylenimine, which distilled at 110-113°, was 232 grams (66% of theoretical).

**Preparation of 1 Amino-hexamethylenimine.** To a standard taper 24/40 three neck, three liter flask was added 1.8 liters of dry ether and lithium aluminium hydride (68.8 grams, 1.81 moles). The flask was equipped with a condenser, a mechanical stirrer, and a 500 milliliter dropping funnel. Into the dropping funnel was put 1-nitrosohexamethylenimine (232 grams, 1.8 moles) and 453 milliliters of ether. Approximately 10% of the solution in the dropping funnel was added to the flask all at once. The solution was brought to reflux by use of a electric heating mantle and the remainder of the nitroso was added at such a rate as to maintain reflux conditions without heating. After the addition was complete the solution was allowed to stand at room temperature for seven hours.

At the end of this period 50 milliliters of water and then 40 milliliters of 40% sodium hydroxide were slowly added. More water was added to the ethereal lithium aluminium hydride solution until
all the remaining lithium aluminium hydride had reacted. The solution was suction filtered and the ether filtrate dried over potassium hydroxide for eight hours. The ether was evaporated on a steam bath and the residue distilled at reduced pressure. The yield of 1 aminohexamethylenimine, which was collected as a colorless liquid at 66-70°C Centigrade (15 mm Hg.), was 80.5 grams (39% of theoretical).

**Preparation of diethyl N-hexamethylenimine phosphoramidate.**

To a standard taper 19/22 three neck, 500 milliliter flask, equipped with a thermometer and a 100 milliliter dropping funnel, was added diethyl phosphite (50.2 grams, 0.36 mole), carbon tetrachloride (56 grams, 0.36 mole) and 91 milliliters of dry xylene. The flask was placed in an ice bath and stirred with a magnetic stirrer. The dropping funnel was used to add 1 aminohexamethylenimine (33.8 grams, 0.727 mole) to the flask at such a rate that the temperature of the solution did not exceed 40°C Centigrade. After the addition was complete the solution was cooled and stirred for an additional hour.

The solution was vacuum filtered and 52 grams (impure) of 1 aminohexamethylenimine hydrochloride was obtained. The filtrate was evaporated under reduced pressure on a rotary evaporator. The residue, 80.3 grams of impure phosphoramidate, was used without distillation since it was found that much of the residue decomposed to tar upon distillation.

**Preparation of 4 n-butyl-1-hexamethyl-5-one-2:1:2:4-3-oxotriazolidinium hydroxide inner salt.** To a standard taper 19/22
three neck, 500 milliliter flask, equipped with a 100 milliliter
dropping funnel and a magnetic stirrer, was added 300 milliliters of
dry benzene and 50% of sodium hydride (15.44 grams, 0.32 mole). The
impure diethyl N-hexamethylenimine phosphoramidate, 80.34 grams, was
slowly added to the flask by means of the dropping funnel. It was
allowed to react overnight. During this time hydrogen was evolved.

The flask was placed in an ice bath and equipped with a
thermometer, a calcium chloride tube, a magnetic stirrer, and a
glass tube fitted through a rubber stopper. The glass tube was
connected to a tank containing dry nitrogen, with the end of the
tube positioned above the liquid, and the flask was flushed with
nitrogen. The glass tube was then connected to a flask containing
dry ice and, with the end of the tube placed below the surface of
the liquid, carbon dioxide was slowly bubbled through the solution
at such a rate that the temperature did not exceed 10° Centigrade.
When the exothermic reaction was complete, the flask was allowed to
come to room temperature and n-butyl isocyanate (32 grams, 0.32
mole) was added all at one time. The flask was flushed again with
dry nitrogen, sealed, and allowed to stand for two weeks.

At the end of this period the solution was filtered and
approximately 80% of the solvent was evaporated at reduced pressure.
The remaining solution was cooled and 100 milliliters of heptane
added to precipitate the ylid. The solution was filtered and the
filtrate evaporated to approximately 15% of the original reaction
volume. More ylid was precipitated by cooling and adding more
heptane. The solution was filtered and the solids combined. The solid material was recrystallized three times from 300 milliliters of carbon tetrachloride to give the purified product. The purified product, consisting of white platelets melting at 123-125°C Centigrade, weighed 17.8 grams (33% of theoretical yield). The infrared spectrum of the ylid contained strong bands at 1650 and 1790 cm⁻¹.

Anal. Calcd. for C₁₂H₂₁N₃O₂: C, 60.22; H, 8.84. Found: C, 59.72; H, 8.84.

Rearrangement of 4-n-butyl-1-hexamethyl-5-one-Δ²-1:2:4-3-oxatriazolidium hydroxide inner salt. The ylid (5.0 grams) was placed in a standard taper 19/22, 50 milliliter flask. The flask was connected to a distilling condenser to collect vapors given off during the heating. The flask was heated at 170-180°C Centigrade for 15 minutes. The white crystalline ylid was changed by the heating to a light yellow oil. The purified product, which distilled at 158-162 (0.5 mm Hg.), weighed 3.3 grams (66% of theoretical yield). Once distilled, the product crystallized to give a white solid, melting point 34-35°C Centigrade. The infrared spectrum of the product, 9-n-butyl-3,10-dione-1a,7a,9a-triazobicyclo [5.2.0] decane, showed a strong absorption band at 1680 cm⁻¹ with an overtone at 1750 cm⁻¹.

Anal. Calcd. for C₁₂H₂₁N₃O₂: C, 60.22; H, 8.84; N, 17.56. Found: C, 59.72; H, 8.84; N, 17.20.

Attempted hydrolysis of 9-n-butyl-3,10-dione-1a,7a,9a-triazobicyclo [5.2.0] decane. The triazole, 9-n-butyl-3,10-dione-1a,
7a,9a-triazobicyclo[5.2.0]decane, was placed in a 19/25 standard taper 50 milliliter flask with a solution consisting of 12 milliliters of concentrated hydrochloric acid, 5 milliliters of water, and 5 milliliters of ethanol. The flask was fitted with a condenser and brought to reflux by use of a heating mantle. After one day at reflux the solvent was removed by evaporation. The infrared spectrum taken of the residue showed it to be essentially the same as the starting material.

In another run under the same conditions, the refluxing was continued for an additional two days. The solution at this time had darkened substantially. The solvent was removed by evaporation under reduced pressure on a rotary evaporator. The residue was dissolved in benzene and made basic by adding alcoholic potassium hydroxide. After filtration, the solution was dried over potassium hydroxide for eight hours, filtered and the filtrate distilled. When the temperature reached 80° Centigrade, the distillation was stopped and a sample of the distillate chromatographed on a Beckmann G.C.-2A gas chromatograph. It was found that the sample consisted of three fractions, two of which were large and one minute. The two large fractions were identified as benzene and ethanol by comparison of their retention time with that of a known sample.

The distillate was acidified with concentrated hydrochloric acid and the solvent removed by evaporation under reduced pressure on a rotary evaporator. A very minute amount of solid remained
which was identified by means of its infrared spectrum as n-butylamine hydrochloride.

Additional attempts to isolate other products from the residue were unsuccessful.

Attempted reduction of the N—N bond in 9-n-butyl-8,10-dione-1a,7a,9a-triazobicyclo[5.2.0]decane. The triazole, 9-n-butyl-8,10-dione-1a,7a,9a-triazobicyclo[5.2.0]decane (5.0 grams, 0.02 mole) was placed in a Parr reaction flask with a small amount of Raney nickel catalyst. The sample was dissolved in 200 milliliters of ethanol and the solution placed in a Parr low pressure hydrogenation apparatus. After seven days at 60 p.s.i. hydrogen pressure, the solution was filtered and the solvent removed by evaporation under reduced pressure on a rotary evaporator. The triazole was found unchanged.

Reduction was then attempted with a Parr high pressure hydrogenation apparatus. The triazole was placed in the reaction vessel with a small amount of palladium on charcoal catalyst and 200 milliliters of ethanol. After three days at 1000 p.s.i. and 150º Centigrade, the solution was filtered and the ethanol removed by evaporation under reduced pressure. The starting material was essentially unchanged.
RESULTS AND DISCUSSION

The six membered ring ylid, 4 n-butyl-1-hexamethyl-5-one-\(\Delta^2\)-1:2:4:3-oxatriazolidium hydroxide inner salt (20), was synthesized via the reactions shown in Scheme III. The starting materials:

Scheme III

\[
\begin{align*}
(C_2H_5O)_2P^+ & \quad \text{NH}_2^- + CCl_4 & \rightarrow & (C_2H_5O)_2P^+ \quad \text{NH}_2^- \quad + \quad CHCl_3 \\
(25) & \quad (26) & \quad (27) & \\
(C_2H_5O)_2P & \quad \text{NH}_2 & \quad + \quad CO_2 & \rightarrow & \left[ (C_2H_5O)_2P^+ \quad \text{NH}_2^- \quad \text{O-CO} \right] \\
(28) & \quad & & \\
(C_2H_5O)_2P^+ & \quad \left[ \text{N-N=C=O} \right] & \quad \text{C}_4\text{H}_9\text{N=C=O} & \rightarrow & \left[ \text{N-N=C=O} \text{N-C=O} \right] \\
(29) & \quad & & \\
\end{align*}
\]

N-aminopiperidine (26), diethylphosphite (25), and carbon tetrachloride reacted to give diethyl N-pentamethylenimine phosphoramidate (27), N-aminopiperidine hydrochloride and chloroform. The
phosphoramidate anion (28) was prepared by reacting the phosphoramidate with sodium hydride to remove a proton from the nitrogen. The anion (28) was then reacted with carbon dioxide to give N-pentamethyleneimine isocyanate (29) which reacted with n-butyl isocyanate to give the N—N ylid. The infrared spectrum of the ylid contained strong bands at 1800 and 1680 cm.⁻¹, which is consistent with previously prepared ylids of this type.⁹

The six members ring ylid (30) was heated at temperatures ranging from 170° to 200° Centigrade in various attempts to obtain the product (31) resulting from a simple 1,2 shift. The ylid was heated until the two carbonyl bands in the infrared spectrum of 1800 and 1680 cm.⁻¹ converged to one band at 1710 cm.⁻¹. None of the product (31) resulting from a simple 1,2 shift could be isolated. In all cases the final heated material appeared to be polymeric in that it was a thick viscous oil that could not be distilled. Attempts to recrystallize it resulted only in the isolation of a very small amount of material identified as starting material. Perhaps instead of a simple 1,2 shift, a ring opening occurred when the ylid was
heated to give an isocyanate polymer (32) as shown in Scheme IV. No attempt, however, was made to confirm the structure of the final gummy material.

Scheme IV

The seven membered ring ylid, 4-n-butyl-1-hexamethyl-5-one-Δ²-1:2:4-3-oxotriazolidium hydroxide inner salt (40) was prepared by means of the reactions shown in Scheme V. The starting material hexamethyleneimine (33), was nitrosoated and reduced to give N-aminohexamethyleneimine (35). The phosphoramidate synthesis was used to prepare N-hexamethyleneimine isocyanate (39), which dimerized in situ with n-butyl isocyanate to give the mixed dimer (40). The ylid showed strong typical bands in its infrared spectrum at 1790 and 1650 cm⁻¹.
The ylid (40) was rearranged by heating it for fifteen minutes at 170-180° Centigrade. The rearranged material (41) was isolated as a distillable liquid, which crystallized after distillation.
Attempts were made to hydrolyze the rearranged material (41) with hydrochloric acid to obtain octahydro-1,2-diazocine (42) and n-butylamine (43). This reaction was unsuccessful in that only a very minute amount of n-butylamine hydrochloride was obtained and none of the cyclic hydrazine (42) could be isolated from the tarry product.

Reduction of the N—N bond in 9,n-butyl-8,10-dione-1α,7α,9α-triazobicyclo[5.2.0]decane (41) was attempted. A low pressure (60 p.s.i.) hydrogenation apparatus was used with Raney nickel catalyst. A high pressure (1000 p.s.i.) hydrogenation bomb was also used with palladium on charcoal catalyst. In both attempts the starting material was isolated unchanged.
CONCLUSIONS

In conclusion it has been shown that 4-n-butyl-1-hexamethylene-5-one-\(\Delta^2\)-1:2:4-3-oxatriazolidinium hydroxide inner salt \((40)\) will readily rearrange under very mild conditions to form the product resulting from expansion of the ring from seven to eight members. However when rearrangement of 4-n-butyl-1-pentamethylene-5-one-\(\Delta^2\)-1:2:4-3-oxotriaxolidium hydroxide inner salt was attempted, even under the most severe conditions, none of the rearranged product \((31)\), resulting from the six membered ring expanding to form the seven membered ring, could be isolated.

The fact that the seven membered ring ylid \((40)\) will rearrange to give a distillable product and not resinous material shows that the mechanism is intramolecular and not intermolecular. It is unlikely that a change in mechanism occurs in the case of the six membered ring even though a distillable product cannot be isolated. In this case decomposition to isocyanates and their sequential polymerization was the final result.

If during the intramolecular rearrangement the migrating group is able to rearrange trans, the intramolecular rearrangement should be allowed in the six membered ring ylid \((30)\), since hexahydro-1,2-diazepine derivatives \((44)\) are known.\(^{10}\) Such is not the case, and therefore, this mechanism does not explain why the six membered ring ylid does not undergo ring expansion.
If the migration is cis, the migrating group remains in the same plane during the rearrangement. If this is the correct mechanism then a trans hexahydro-1,2-diazepine derivative (n=3) would represent the transition state during a rearrangement of the six membered ring ylid and a trans octahydro-1,2-diazocine derivative (n=4) represents the transition state during the rearrangement of the seven membered ring ylid.

The reason that the six membered ring ylid does not form the seven membered ring derivative is that trans hexahydro-1,2-diazepine (45) is sterically strained. Evidence for this may be inferred from
the fact that trans-cyclooctene (46) is the smallest cycloalkene prepared thus far in the trans configuration. Trans cycloheptane, the carbocyclic analogue of hexahydro-1,2-diazepine (45) is not known.

Additional work completed after this thesis was begun has shown that 1-tetramethylene-5-one-Δ²-1:2:4-3-oxotriazolidium hydroxide inner salt (47) also decomposes when heated to form a polymeric product.

As with the six membered ring ylid, the five membered ring ylid does not undergo ring expansion due to the ring strain that would occur during the transition state. This fact gives additional proof for the proposed cis migration.
LITERATURE CITED