

AN ABSTRACT OF THE THESIS OF

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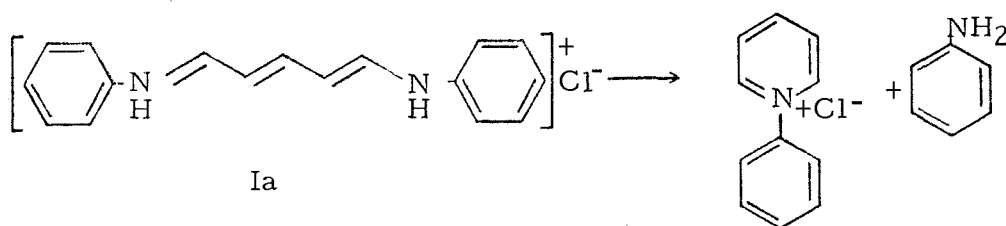
Title: STUDIES ON THE MECHANISM OF FORMATION OF  
N-PHENYLPYRIDINIUM SALTS FROM 1,7-DIAZA-1,3,  
5-HEPTATRIENES

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Abstract approved: \_\_\_\_\_

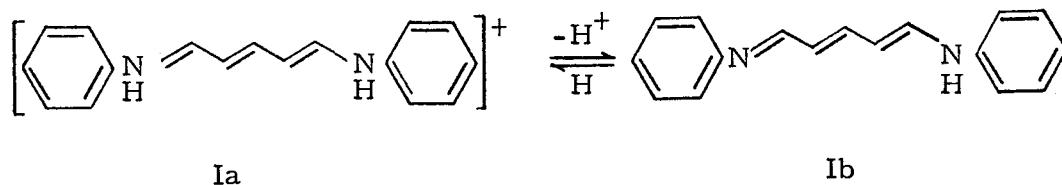
Elliot N. Marvell

The mechanism of the ring closure of 1,7-diphenyl-1,7-diaza-1,3,5-heptatriene (Ia) to phenylpyridinium chloride and aniline was investigated. The ring closure proceeds smoothly and



quantitatively in a variety of media and is free from measurable side reactions. In anhydrous methanol, ring closure of Ia proceeds with approximate first-order kinetics,  $k \approx 6 \times 10^{-6} \text{ sec}^{-1}$  at  $40^\circ$ , and can be readily followed by U. V. -vis. spectroscopy.

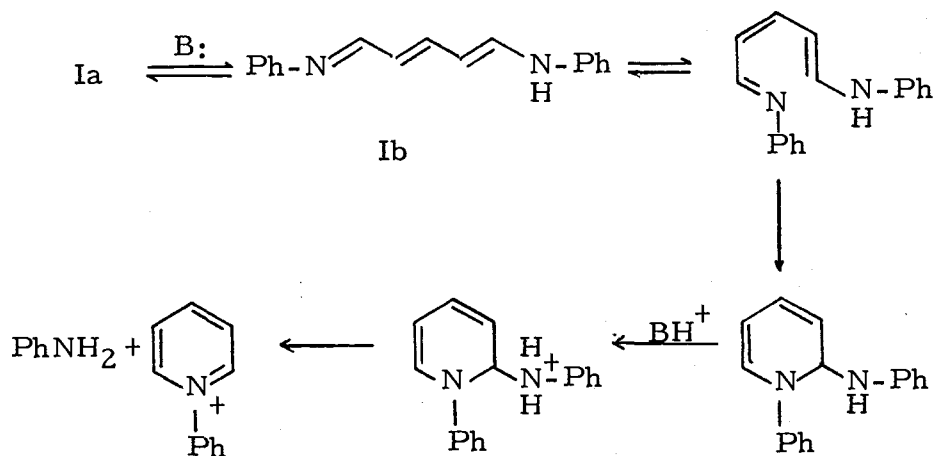
In methanol, Ia is in facile equilibrium with Ib, ( $K_{eq} = 5 \times 10^{-7}$  M at  $25^{\circ}$ ) to which it can be easily converted by addition of a



base such as triethylamine, tri-n-butylamine or sodium methoxide.

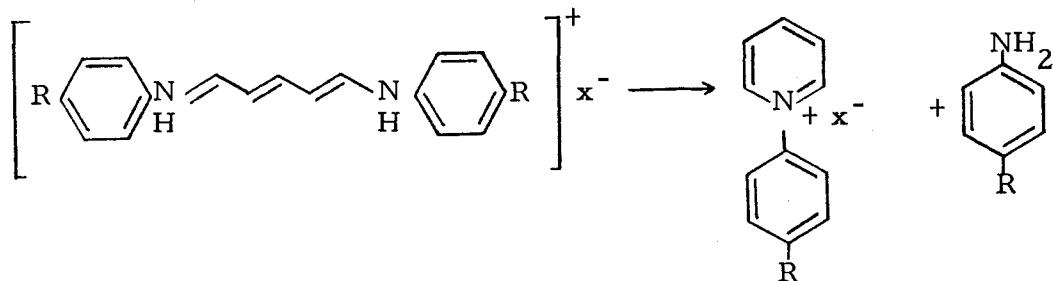
The bases produce a notable catalytic effect on the rate of ring closure. Addition of one equivalent of base produces a large increase in rate, but when a sufficient amount of base is added to convert all of Ia to Ib, the rate becomes independent of the nature and concentration of the added base. The same final rate is reached with each of the bases mentioned above. Thus the function of the added bases is to convert Ia to the reactive intermediate Ib which then undergoes ring closure. In the presence of excess base, the ring closure shows clean first-order kinetics,  $k = 3.5 \times 10^{-4} \text{ sec}^{-1}$  at  $40^{\circ}$  in methanol. The rate of reaction increases mildly as the solvent is changed from methanol to methanol-dioxane mixtures. An increase of 4.8 fold is observed when the mixture reaches 80% dioxane-20% methanol. Similarly, when the reaction is transferred from methanol to acetone, a six fold increase in rate is observed.

All these data are conveniently accommodated by the following mechanism:



**Ia** is assumed to have the all-trans configuration, but changes in configuration are expected to be rapid in the media studied. The acid catalyzed loss of aniline is not expected to be rate-determining, since addition of benzoic acid does not bring about any acceleration in rate. Thus the valence isomerization step is assumed to be rate-determining.

Six symmetrically substituted derivatives of **Ia** were prepared and the rate of their ring closures in the presence of excess



triethylamine in methanol were determined. The ring closures proceed with first-order kinetics and results in the formation of para-substituted phenylpyridinium halides and para-substituted anilines in near quantitative yields. The rate data, summarized in the table below indicate that to a large degree the reaction is

TABLE Ia. First-order rate constants and activation parameters for ring closure of Ia and II in presence of excess triethylamine in methanol.

| R                                | x  | $k \times 10^4 \text{ sec}^{-1}$<br>@ 40°C | $\Delta H^\ddagger \pm 1 \text{ kcal}$<br>@ 30° | $\Delta S^\ddagger \pm 1$ |
|----------------------------------|----|--|---|---------------------------|
| H                                | Cl | 3.52                                       | 22.7  | 0.0                       |
| CH <sub>3</sub>                  | Cl | 3.11                                       | 22.8  | 0.2                       |
| OCH <sub>3</sub>                 | Cl | 3.65                                       | 22.0  | -1.3                      |
| Cl                               | Cl | 6.22                                       | 22.7  | 0.9                       |
| F                                | Cl | 5.23                                       | 22.3  | -0.3                      |
| N(CH <sub>3</sub> ) <sub>2</sub> | Cl | 2.53                                       | 22.6  | -1.0                      |
| NO <sub>2</sub>                  | Br | 12.0                                       | 22.7  | -0.2                      |

insensitive to substituent effects, in general accord with the proposed valence isomerization mechanism.

Studies on the Mechanism of Formation of  
N-Phenylpyridinium Salts from  
1,7-Diaza-1,3,5-Heptatrienes

by

Iraj Khatib Shahidi

A THESIS

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Dean of Graduate School

Date thesis is presented July 8, 1969

Typed by Maryolive Maddox for Iraj Khatib Shahidi

## ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. E. N. Marvell for his patience and guidance during the course of this work.

To Lily



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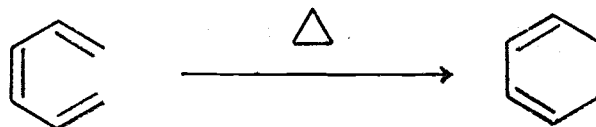
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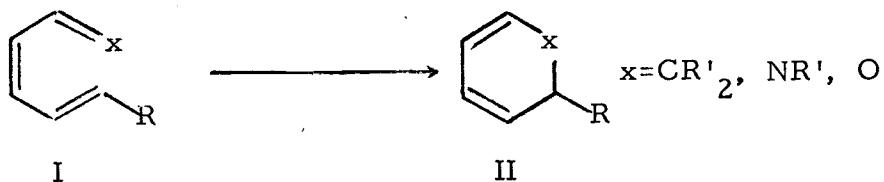
STUDIES ON THE MECHANISM OF FORMATION OF  
 N-PHENYLPYRIDINIUM SALTS FROM  
 1,7-DIAZA-1,3,5-HEPTATRIENES

INTRODUCTION

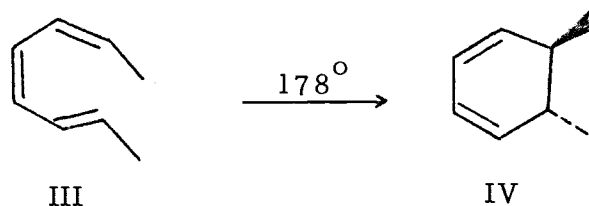
Valence isomerization reactions have recently become the focus of renewed attention. Typical of these reactions is the thermal rearrangement of cis-hexatrienes to cyclohexadienes.



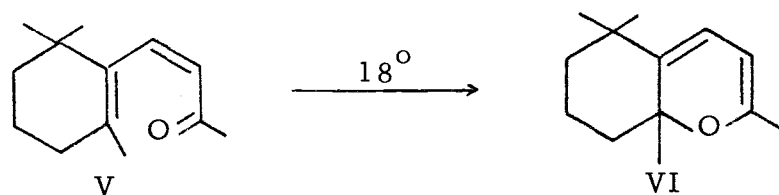
Interest in this laboratory in the thermal rearrangement of above type compounds originated from work on the Claisen rearrangement and has extended to thermal isomerization of trienes of the



type I where X could be carbon, nitrogen or oxygen. Thus for example, Marvell, Caple and Schatz (31) found that triene III isomerizes to IV at  $178^\circ$  with a first-order rate constant of



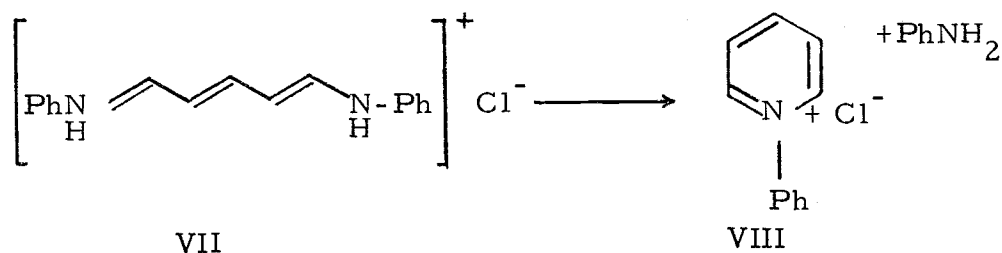
$2.2 \times 10^{-5} \text{ sec}^{-1}$ . Marvell and co-workers (35) also found that the cis-dienone V is converted to the  $\alpha$ -pyran VI at  $18^\circ$  with a rate constant of  $1.4 \times 10^{-3} \text{ sec}^{-1}$ .



Extrapolated to a common temperature, the rate for the dienone is ca. seven powers of ten greater than that of the carbon system (III). This difference in reactivity might be rationalized in two ways. The higher electronegativity of oxygen compared to carbon leads to a polarization of the carbon-oxygen double bond and the positive centers are at carbons one, three and five. Thus reaction of the negative oxygen with the positive carbon at C<sub>5</sub> could account for the observed reactivity. A more remote possibility is that the oxygen atom could utilize one of its pairs of unshared

electrons in the formation of the new bond during the ring closure. If the former reasoning were correct, the nitrogen system would be expected to show a reactivity intermediate between the carbon and oxygen systems. On the other hand, if the latter explanation were true, the reactivity of the nitrogen system would be expected to be comparable to that of the oxygen system.

Since no previous studies of valence isomerizations in the nitrogen system have been published, a study of mechanism and reactivity of dienimines seemed of considerable interest. Since synthesis of trienes of the type I with  $X=NH$ ,  $NR'$  poses a number of experimental difficulties, a study of the well-known ring

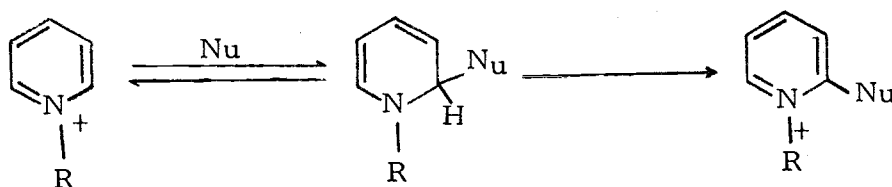


closure of triene VII to phenylpyridinium chloride (VIII) and aniline (25, 46) was chosen. This reaction has been known for over 60 years, but its mechanism has not been previously investigated. Since one possible pathway for the ring closure could be through valence isomerization, a study of its mechanism was initiated.



## HISTORICAL

The pyridine ring loses its characteristic stability when quaternized and becomes susceptible to attack of various nucleophilic reagents. These reactions have recently received considerable attention, in part due to their bio-chemical importance (5, p. 301-349; 27, p. 166-180). The pyridinium ion is so susceptible to the above type attack that even relatively weak nucleophiles such as hydroxide ion or cyanide ion will attack the nucleus (1). The general reaction bears resemblance to the nucleophilic aromatic substitution,  $SN_{Ar2}$  (29). The reaction will result in

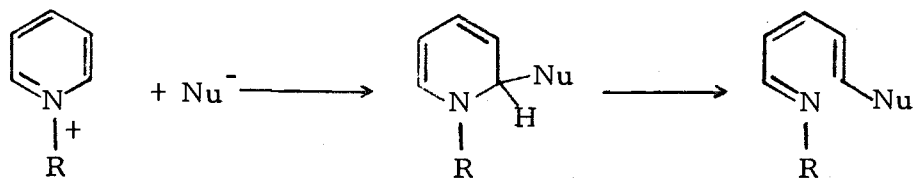


substitution only if a hydride ion is lost. In the absence of an oxidizing medium this substitution is an unfavorable step and thus the intermediate dihydropyridine can be isolated. As a consequence, the course of the reaction can be studied in a stepwise fashion.

For the reversible addition of nucleophiles the reaction is thermodynamically controlled and addition at the 4-position is

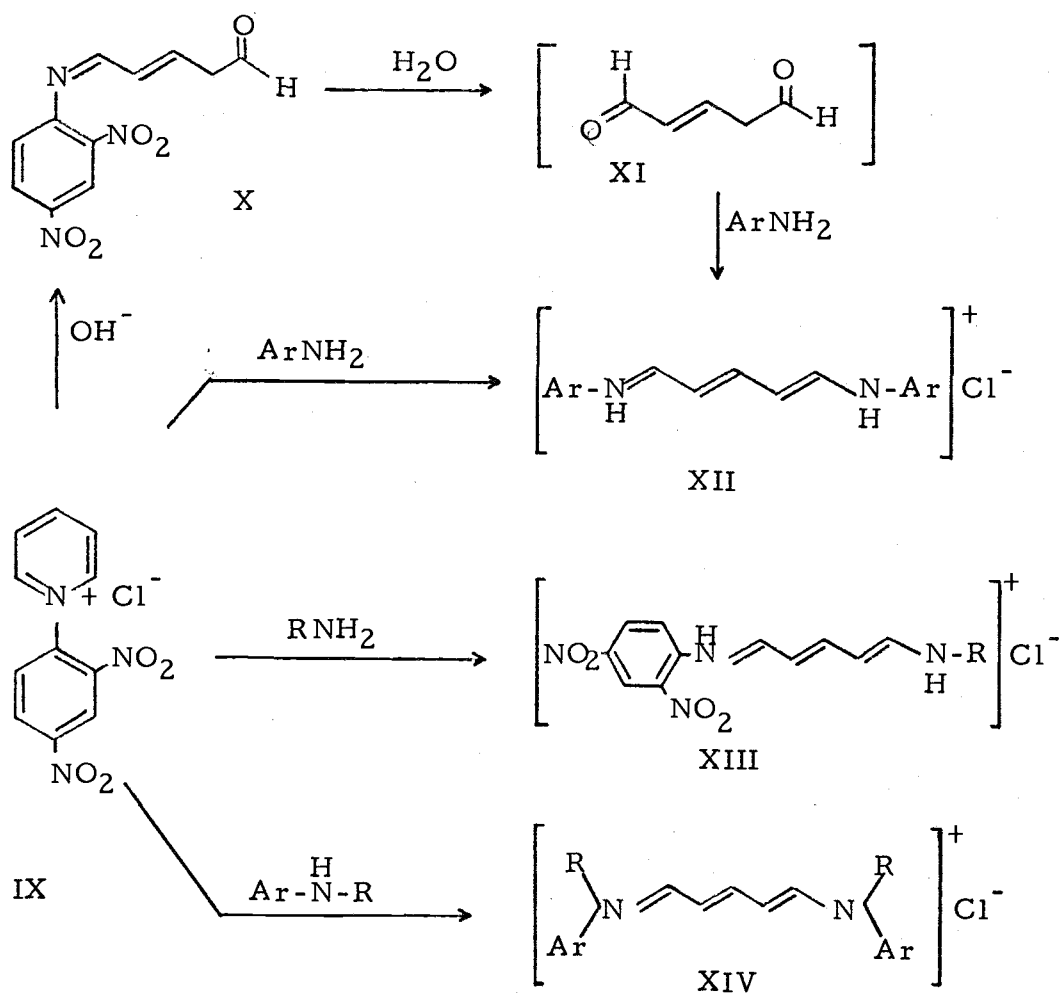
avored over the 2-position, since it has been shown that the  $\pi$ -system ( $C=C-\ddot{N}-C=C$ ) resulting from the former addition is more stable than the ( $C=C-C=C-\ddot{N}-$ ) system formed by the latter (29). An alternate explanation, proposing the initial formation of a charge transfer complex has also been advanced to account for the direction of substitution. In an attempt to summarize the information recorded in the literature relative to the reaction of nucleophiles with pyridinium ions, Kosower (26, 28) related the position of attack of a nucleophile with the possible intermediacy of a charge transfer complex. Thus reactions with nucleophiles which have a low ionization (oxidation) potential were presumed to proceed via a charge transfer complex and to form 1,4-dihydropyridines, others would presumably proceed by attack at the 2-position. For example, attack of cyanide, thiosulfate and active methylenes proceeds by the former route, while the attack of hydroxide ion and aniline follows the latter route (26).

The attack of aliphatic and aromatic amines as well as hydroxide ion on certain pyridinium compounds proceeds with 2-addition followed by ring opening. It appears from the examples studied that the ring opening is promoted by presence of strongly electron withdrawing groups such as cyanide, carbamoyl, and 2,4-dinitrophenyl on the pyridine nitrogen. The reactions of

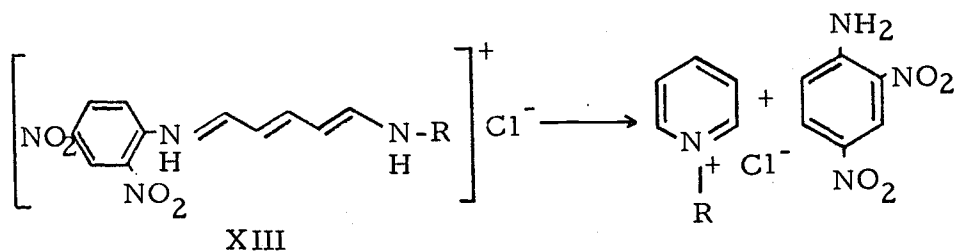
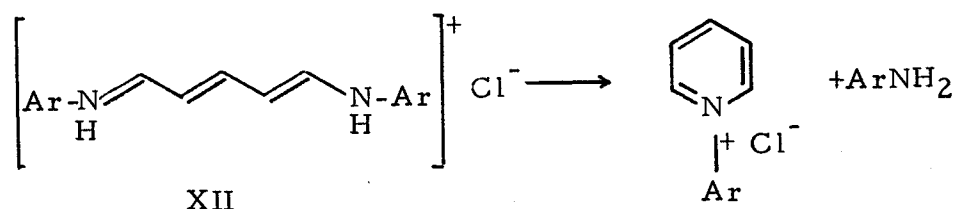


2,4-dinitrophenyl pyridinium chloride (IX) with hydroxide ion and amines were first investigated by Zincke in 1904 (46, 47, 48, 49).

The hydroxide attack leads to ring opening, giving the monoanil



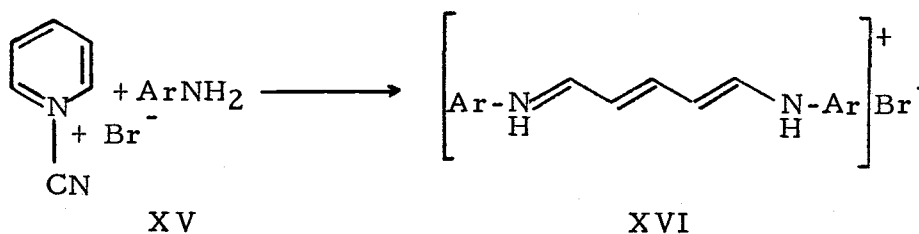
X which upon further hydrolysis gives rise to glutaconaldehyde XI. The most interesting reactions of IX are, however, with aliphatic and aromatic amines which give rise to highly colored anils XIII and dianils XII of the parent glutaconaldehyde. The diazaheptatrienes XII and XIII are essentially reactive intermediates in the over-all conversion of the starting pyridinium compound IX to other pyridinium salts. Thus they readily recyclize by heating directly or in a solvent, or more commonly in presence of acid. The recyclization provides a readily accessible



route to many aryl pyridinium compounds that cannot generally be prepared through direct reaction with pyridine.

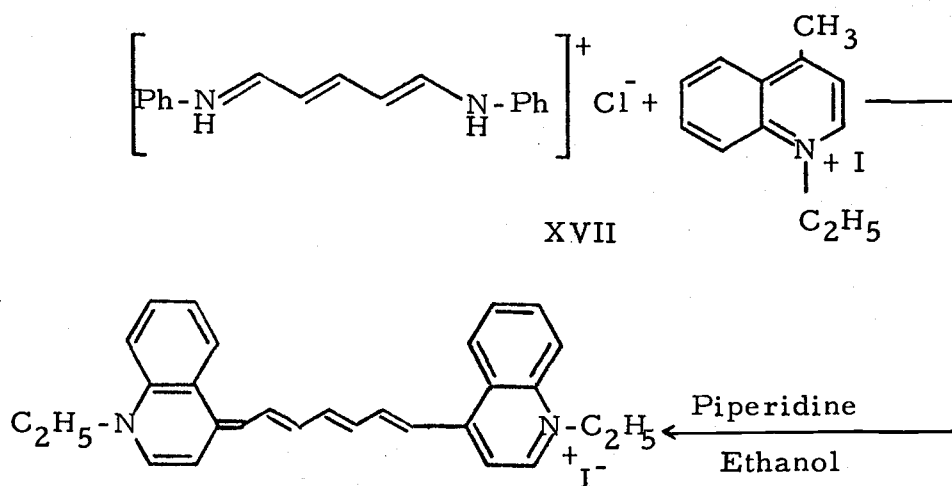
About the time that Zincke was exploring the

2,4-dinitrophenyl pyridinium ring cleavages, König (24, 25) discovered an alternate route to preparation of diazaheptatrienes XVI through the reaction of cyanopyridinium bromide (XV) with

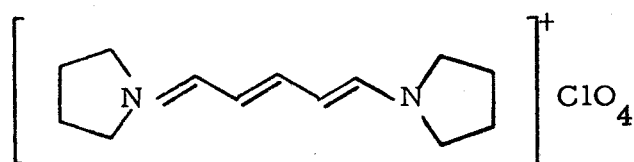


aromatic amines. Cyanopyridinium bromide shows enhanced reactivity compared to IX and subsequently can be reacted with anilines substituted with highly electron withdrawing groups that normally would not be basic enough to attack IX.

The diazaheptatrienes can be readily hydrolyzed to glutaraldehyde which can be used as an intermediate in other synthesis. This feature was utilized in synthesis of many cyanine dyes, where the condensation of diazaheptatrienes with compounds with active methylene groups provided a means for lengthening the polyene chain (17, p. 244-268). An example of such reaction with lepidine ethiodide (XVII) is shown below.

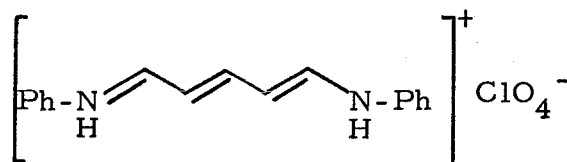


Aside from industrial applications, other features of diazaheptatrienes have also received some attention. Some light has been thrown on the configuration of diazaheptatrienes by X-ray studies of Hoppe and Baumgartner (20) who found that XVIII



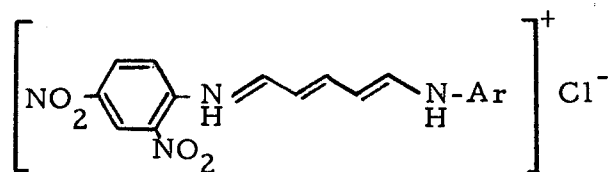
XVIII

exists in the all-trans form in its crystals. Doerr and co-workers (8) were able to show that a photo chemical trans—cis isomerization of XIX can be readily achieved with visible light. After irradiation the compound reverts to its original all-trans form by a thermal process.

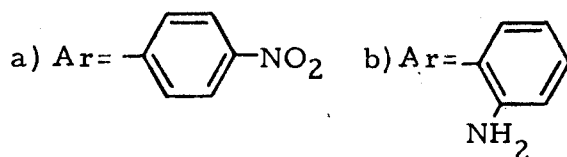


XIX

In recent years Grigor'eva (12, 13, 14, 15, 16) has undertaken an extensive study of the reactions of diazaheptatrienes, and has provided valuable spectral information for a large number of the above compounds and their cyclization and hydrolysis products. Of particular interest is his reported isolation of the unsymmetrical dianils XXa (13) and XXb (12) from the reaction of 2,4-dinitrophenylpyridinium chloride with *p*-nitro aniline and *o*-phenylenediamine, respectively. The unsymmetrical dianils had not been previously isolated, the symmetrical analogs (XII)



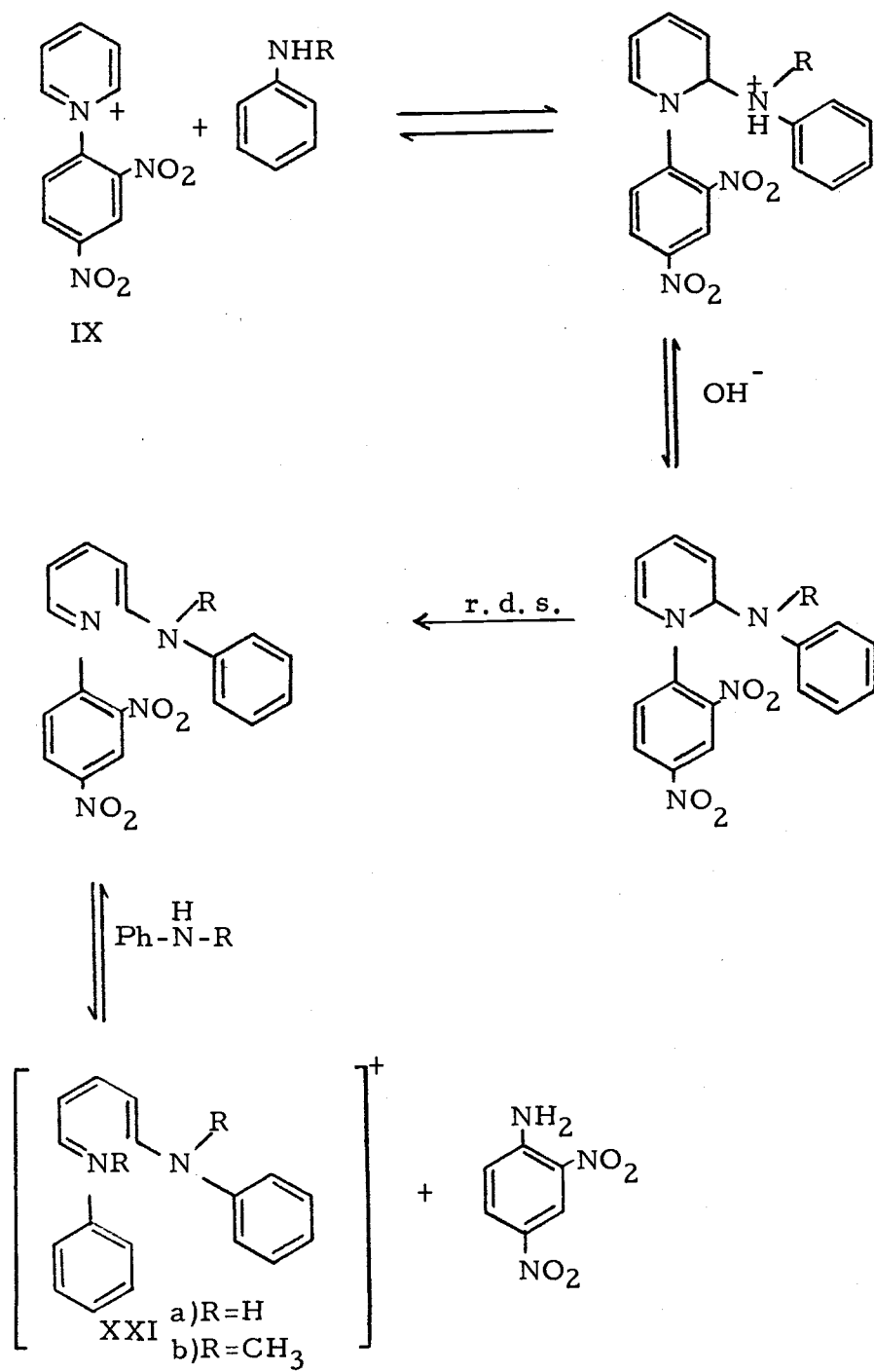
XX



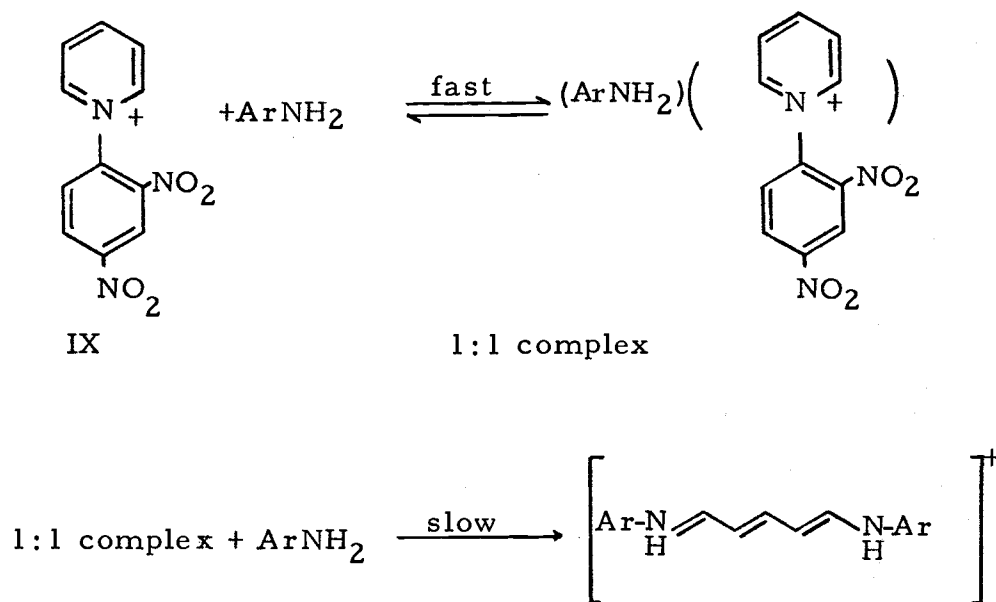
being the initial isolable products of the reaction.

The mechanism of the ring opening of 2,4-dinitrophenyl pyridinium chloride (IX) with aromatic amines was first studied by Van den Dunghen, Nasielsky and Van Laer (10) in 1957. The kinetics of the reaction of IX with aniline and N-methylaniline in 50% aqueous ethanol were investigated, and were found to be first order in IX, the hydroxide ion, and the amines at constant pH, but order 1.5 with respect to amines when the concentration of the amine determined the alkalinity of the medium. The course of the reaction was followed by measuring the absorbance of the symmetrical dianils XXIa and XXIb formed in the reaction; however, the rate constants could not be determined due to experimental difficulties. The following mechanism, involving a rate determining ring-opening step, was proposed (10).





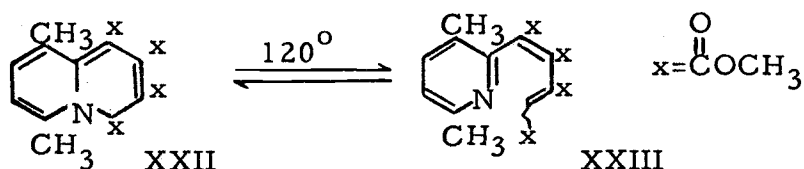
The kinetics of the reaction of IX with a number of meta and para substituted anilines in methanol was also studied by Oda and Mita (36). The kinetics were measured by gravimetric determination of the amount of dianils formed, and the reaction was found to be third-order--second-order in the aniline and first-order in IX. The rate of reaction with aniline itself was  $1.7 \pm 0.2 \times 10^{-2} \text{ l. mole}^{-2} \cdot \text{sec}^{-2}$  at  $30^\circ$ , but contrary to Grigor'eva's findings (13), p-nitroaniline did not react. A Hammett type correlation (18, p. 184) for the reaction showed a  $\rho$  value of  $-4.5$  for the compounds studied. Oda and Mita proposed a mechanism involving a rate determining attack of aniline on a 1:1 complex of IX and the amine. No detailed structure for the complex was



given and therefore the formation of an unsymmetrical dianil (XX) remains a possibility. Oda and Mita also found that when -nitro-phenyl pyridinium chloride is substituted for IX the reaction does not proceed, while when 2,4,6-trinitrophenylpyridinium chloride is employed the dianil formation is overshadowed by direct displacement of pyridine from IX by aniline.

Aside from an indirectly-related study of the ring opening of 1-(N, N-dimethylcarbamoyl)pyridinium chloride by aqueous alkali (22), the two investigations mentioned above appear to be the only mechanistic studies on the reactions of diazaheptatrienes. The mechanism of the recyclization of these compounds, as far as can be ascertained, have not been previously studied.

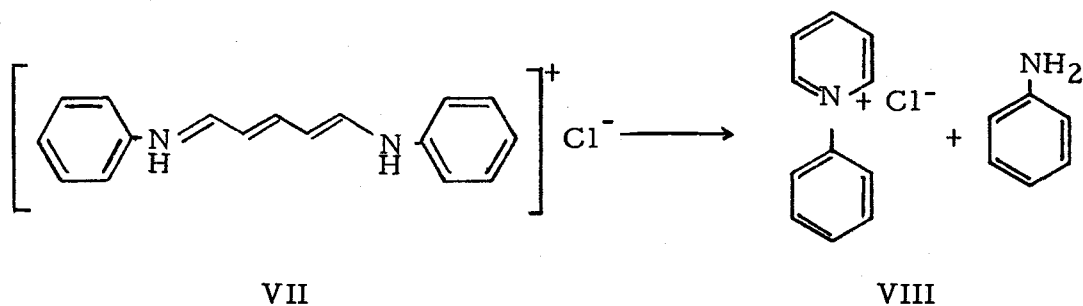
As noted earlier the thermal valence isomerizations of cis-hexatrienes to cyclohexadienes, especially in the case of cyclic trienes, has been amply demonstrated. The valence isomerization of a cis-dienone to an  $\alpha$ -pyran has also been reported (35). The possibility of a similar valence isomerization of dienimines has not as yet been suggested or proven. The recently observed (2) facile interconversion of XXII and XXIII, however, might involve a valence isomerization.



## DISCUSSION

Introduction

The purpose of this study is to determine the mechanism of the ring closure of 1,7-diphenyl-1,7-diaza-1,3,5-heptatriene (VII) to phenylpyridinium chloride (VIII) and aniline. The first



part of the thesis will consider the synthesis of VII, the kinetics of its ring closure, and the possible mechanisms of the reaction. Part two will describe the syntheses and kinetics of ring closure of six symmetrically substituted derivatives of VII. The effect of the substituents on the reaction rate in terms of possible mechanisms will be discussed.

Part OneSynthesis of VII and kinetics of its ring closure

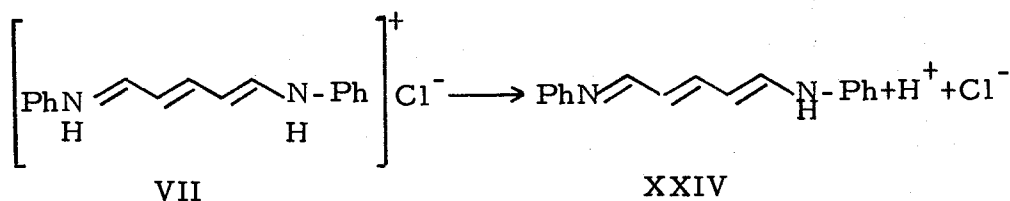
Triene VII was prepared according to Zincke's procedure (46) through the reaction of 2,4-dinitrophenylpyridinium chloride (IX) and aniline in 80% aqueous ethanol. The shiny red crystals of VII melt at 146-147<sup>o</sup>, in close agreement with the value of 143-144<sup>o</sup> reported by Zincke (47). The U.V.-vis. spectrum of the compound also agrees closely with the reported values in the literature (14, 15). Samples of VII prepared by the above procedure are of reasonable purity, as indicated by the absence of any extraneous peaks in the U.V.-vis. spectrum and by the results of the elemental analysis reported by Zincke and others (43, 47).

Zincke reported (47) that VII reacts in hot concentrated hydrochloric acid to give aniline hydrochloride and phenylpyridinium chloride (VIII). Studies in this laboratory (30, 32) showed that ring closure of VII proceeds in a variety of media and does not require added acid. Thus the ring closure of VII in methanol proceeds smoothly and in quantitative yield. Aniline is isolated as its benzanilide derivative in 93% yield and VIII in 110% yield (30). The latter value is always too high, apparently due to the difficulty of removing the solvent. Essentially the same results

are obtained in presence of excess triethylamine in methanol (30) or in 80% dioxane - 20% methanol. Thus the course of the reaction is unaffected by the changes in conditions, and the reaction is free from any complicating side reactions.

The detailed structure of VII is unknown, however, it is most probably in the all-trans or stretched linear form, since X-ray studies (20) on the similar triene XVIII have shown that it exists in the all-trans form in the crystal. This poses the problem that ring closure of VII to VIII and aniline would require a configurational change to convert the all-trans form of VII to one having a cis central double bond. A possible explanation for the coiling process in the media that have been employed will be discussed later in this section.

The U. V.-vis. spectrum of VII in methanol consists of two peaks, a larger peak at 485  $m\mu$  and a smaller one at 407  $m\mu$ . Their relative intensities are concentration dependent, the 407  $m\mu$  peak increasing in intensity as the 485  $m\mu$  peak decreases when the solution is diluted. The above behavior is suggestive of the presence of an equilibrium between VII and a second substance. A reasonable expectation is that a small portion of VII dissociates in methanol to its free base form XXIV and hydrogen chloride. Thus the 485  $m\mu$  peak could be assigned to VII and the 407  $m\mu$ .



peak to XXIV. This hypothesis was verified since addition of excess aniline hydrochloride removed the 407 m $\mu$  peak and increased the 485 m $\mu$  peak, while addition of excess triethylamine led to the disappearance of 485 m $\mu$  peak. In presence of aniline hydrochloride VII has  $\lambda_{\max}$  485 m $\mu$  ( $\epsilon=115,000$ ), while XXIV has  $\lambda_{\max}$  407 m $\mu$  ( $\epsilon=67,000$ ) in presence of excess triethylamine (32). These values agree closely with  $\lambda_{\max}$  485 m $\mu$  ( $\epsilon=127,000$ ) for VII and  $\lambda_{\max}$  406 m $\mu$  ( $\epsilon=65,000$ ) for XXIV in 95% ethanol, as reported by Grigor'eva (14, 15).

Assuming the extinction coefficients to be unchanged in methanol alone, it is possible to measure the equilibrium constant for the dissociation. The value found at 25°C is  $\sim 5 \times 10^{-7}$  m/l, measured at a concentration of  $1 \times 10^{-5}$  M. This value was not measured with a high degree of accuracy since the exact pH of the methanol solution was not ascertained. An attempt to find the pH of the solution by use of indicators (23) encountered experimental difficulties and was not fruitful. Hence the value

reported is based on the assumption that the methanol solution was free from other acids or bases.

The conversion of VII to VIII can be followed by U. V.-vis. spectroscopy, since VII absorbs in the visible while the products absorb in the ultraviolet. The equilibrium between VII and XXIV noted above complicates the measurement, but by adding excess hydrochloric acid to the solution prior to the determination of the concentration, all XXIV is converted to VII. At 40°C the ring closure of VII in methanol proceeds with approximate first-order kinetics with  $k \approx 6 \times 10^{-6} \text{ sec}^{-1}$  (Figure 1). The rate shows a gradual upward drift during the course of the reaction. The plot shown in Figure 1 is for reaction of VII at  $5 \times 10^{-4} \text{ M}$  in methanol in a constant temperature oil bath. The rate was determined by withdrawing aliquots at appropriate intervals and determining the absorbance of the total amount of VII present in the solution as described above. At 60°C, different behaviors are observed when the kinetics are carried out at  $5 \times 10^{-4} \text{ M}$  in the previously described manner (upper curve in Figure 2) or at  $2 \times 10^{-5} \text{ M}$  inside the thermostated cell of the spectrophotometer (lower curve in Figure 2). In the latter case, the rate is measured by following the changes in concentration of VII in equilibrium with a small amount of XXIV. A possible explanation for this disparity



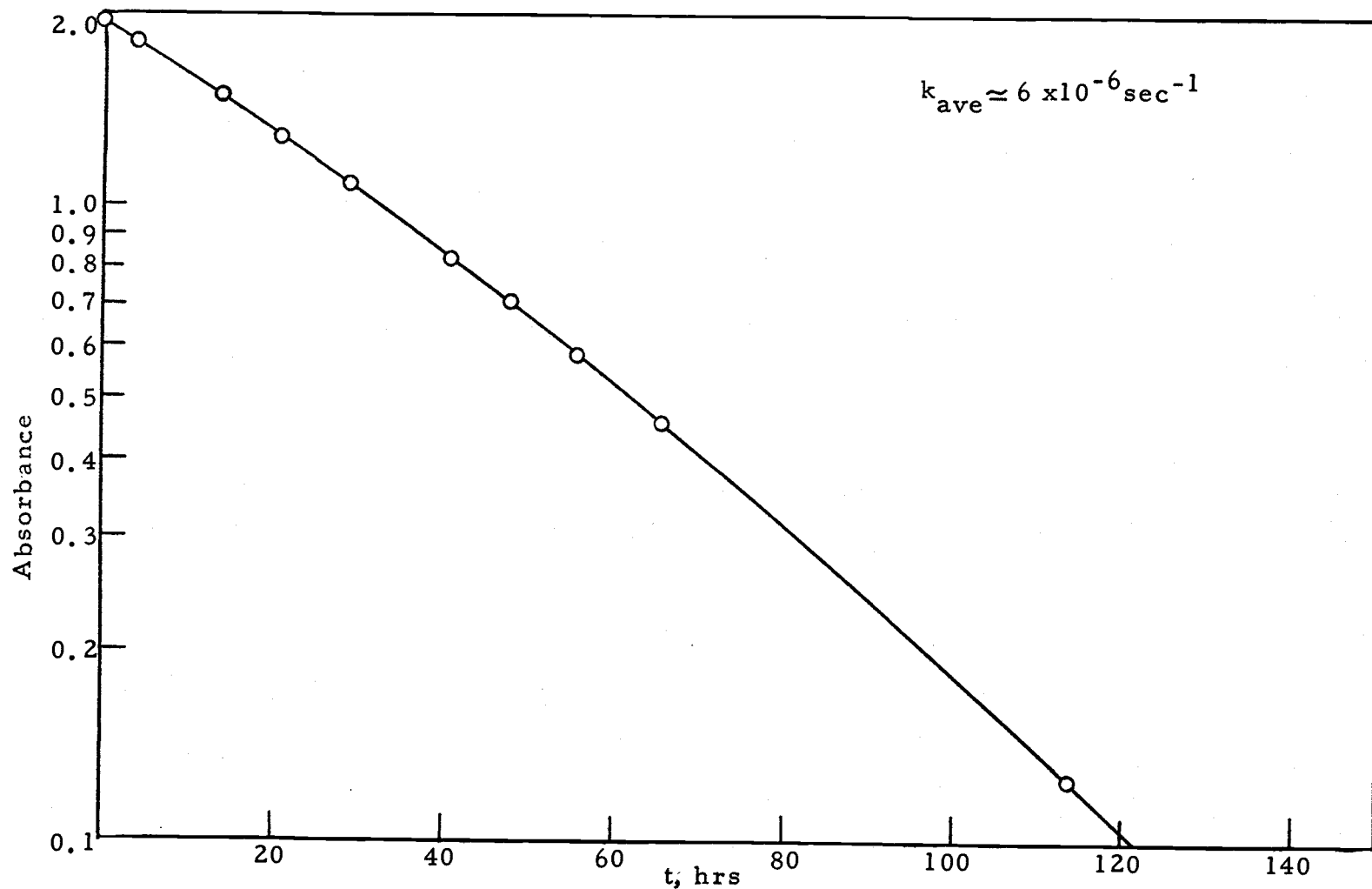


Figure 1. Plot of logarithm of absorbance vs. time for ring closure of VII in methanol.  
 $[\text{VII}] = 5 \times 10^{-4}$ ,  $T = 40^\circ\text{C}$ .

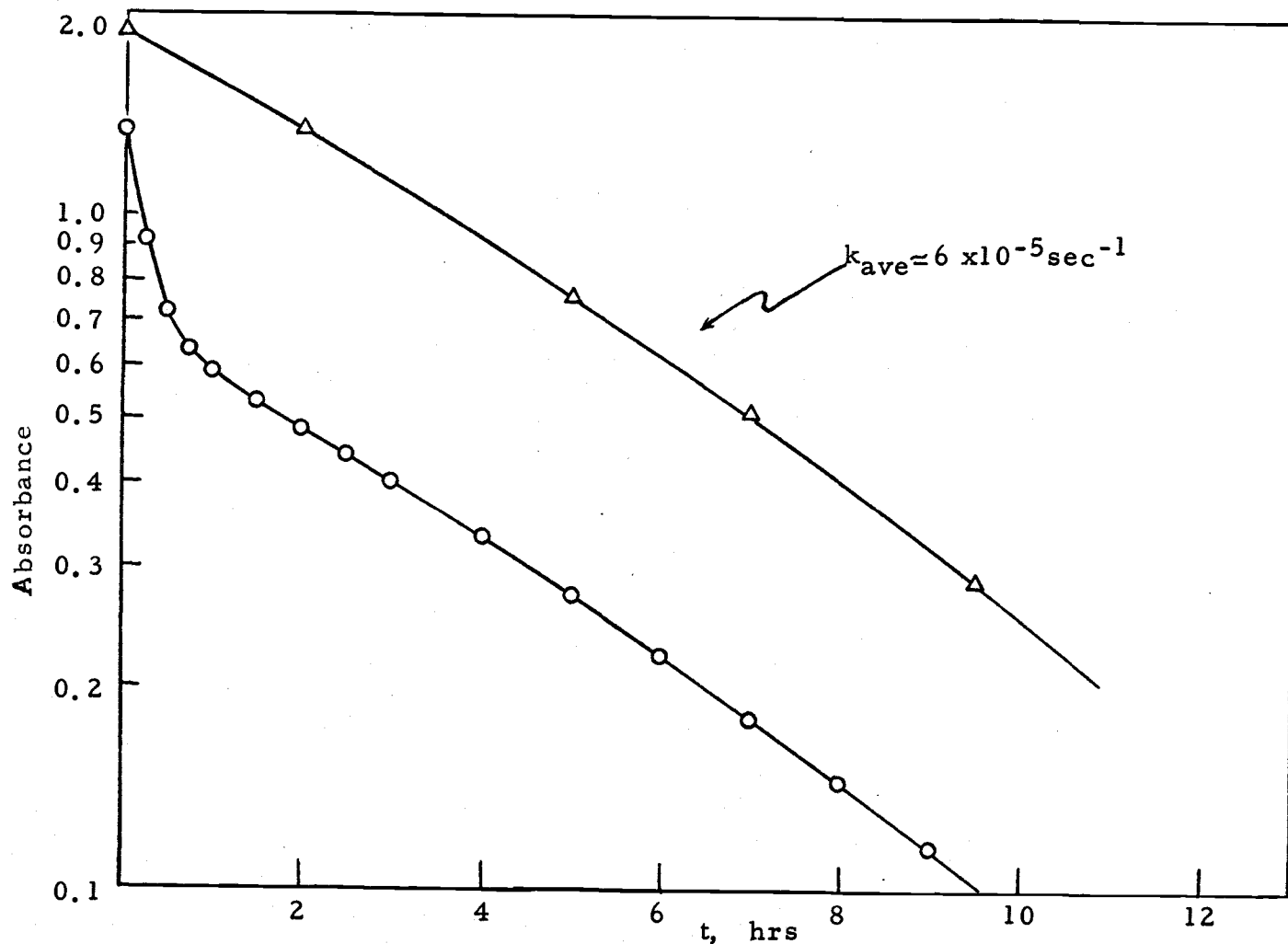


Figure 2. Plots of logarithm of absorbance vs. time for ring closure of VII in methanol. O,  $[VII] = 2 \times 10^{-5} M$ ;  $\Delta$ ,  $[VII] = 5 \times 10^{-4} M$ .  $T = 60^\circ C$ .

will be offered shortly.

The equilibrium between VII and XXIV raised the question of whether one or both are involved in the ring closure. When an equimolar amount of triethylamine, tri-n-butylamine, or sodium methoxide was added to a solution of VII in methanol, a ca. 50 fold increase in rate was observed (32). Thus the reaction showed remarkable susceptibility to base catalysis. Experiments using different concentrations of the added base unveiled a rather interesting relationship between the rate and the base concentration. The rate increased with increasing the concentration of the base when the base concentration was lower than or equal to the concentration of VII (Table I). However, in the presence of excess base the rate was independent of the base concentration (Table II). This rate plateau was reached when the concentration of the base was sufficient to completely convert VII to XXIV (Figure 3). This behavior is, moreover, independent of the nature of the base, resulting in identical rates with excess triethylamine, tri-n-butylamine and sodium methoxide (Table II). In presence of excess triethylamine, the rate constant for the ring closure of VII in methanol is  $3.5 \times 10^{-4} \text{ sec}^{-1}$  at  $40^\circ$ , which should be compared with the value of  $6 \times 10^{-6} \text{ sec}^{-1}$  in the absence of the base. Furthermore, with excess base the rates show clean first-order

TABLE I. First-order rate constants for ring closure of VII in methanol in presence of added bases.

$[\text{VII}] = 2.0 \times 10^{-5} \text{ M}$       Temp:  $40^\circ \text{C}$

| Run No. | Added Base       | $[\text{Base}] \times 10^5 \text{ M}$ | $k \times 10^4 \text{ sec}^{-1}$ |
|---------|------------------|---------------------------------------|----------------------------------|
| 1       | Sodium Methoxide | 0.4                                   | 0.31                             |
| 2       | " "              | 1.0                                   | 1.96                             |
| 3       | " "              | 2.0                                   | 3.24                             |
| 4       | Triethylamine    | 0.4                                   | 0.33                             |
| 5       | "                | 1.0                                   | 1.80                             |
| 6       | "                | 2.0                                   | 2.68                             |
| 7       | "                | 100.0                                 | 3.47                             |
| 8       | Tri-n-butylamine | 0.4                                   | 0.27                             |
| 9       | "                | 1.0                                   | 1.50                             |
| 10      | "                | 2.0                                   | 2.58                             |

TABLE III. First-order rate constants for the ring closure of VII in methanol in presence of excess bases, at  $39.2^\circ \text{C}$ . (30)

| Run No. | $[\text{VII}] \times 10^5 \text{ M}$ | Added Base       | $[\text{Base}] \times 10^5 \text{ M}$ | $k \times 10^4 \text{ sec}^{-1}$ |
|---------|--------------------------------------|------------------|---------------------------------------|----------------------------------|
| 1       | 2.0                                  | Sodium Methoxide | 2.4                                   | 2.35                             |
| 2       | 2.0                                  | " "              | 4.8                                   | 2.97                             |
| 3       | 2.0                                  | " "              | 12.0                                  | 3.04                             |
| 4       | 2.0                                  | " "              | 24.0                                  | 3.04                             |
| 5       | 2.0                                  | " "              | 240.0                                 | 3.06                             |
| 6       | 2.0                                  | Triethylamine    | 5.9                                   | 2.96                             |
| 7       | 2.0                                  | "                | 11.7                                  | 3.08                             |
| 8       | 2.0                                  | Tri-n-butylamine | 10.9                                  | 3.05                             |
| 9       | 2.0                                  | "                | 21.8                                  | 3.08                             |

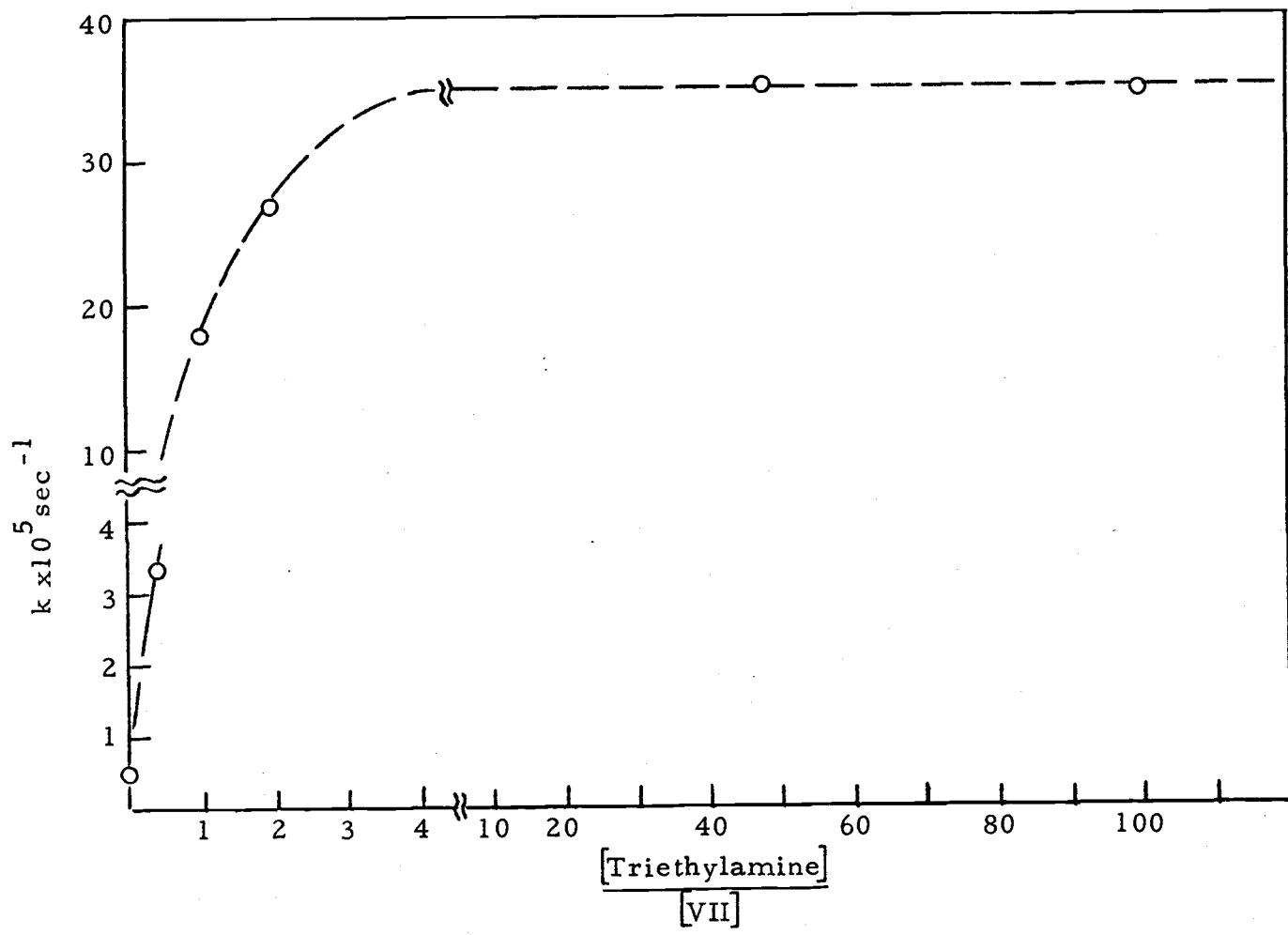


Figure 3. Plot of the first-order rate constants vs. the added triethylamine.

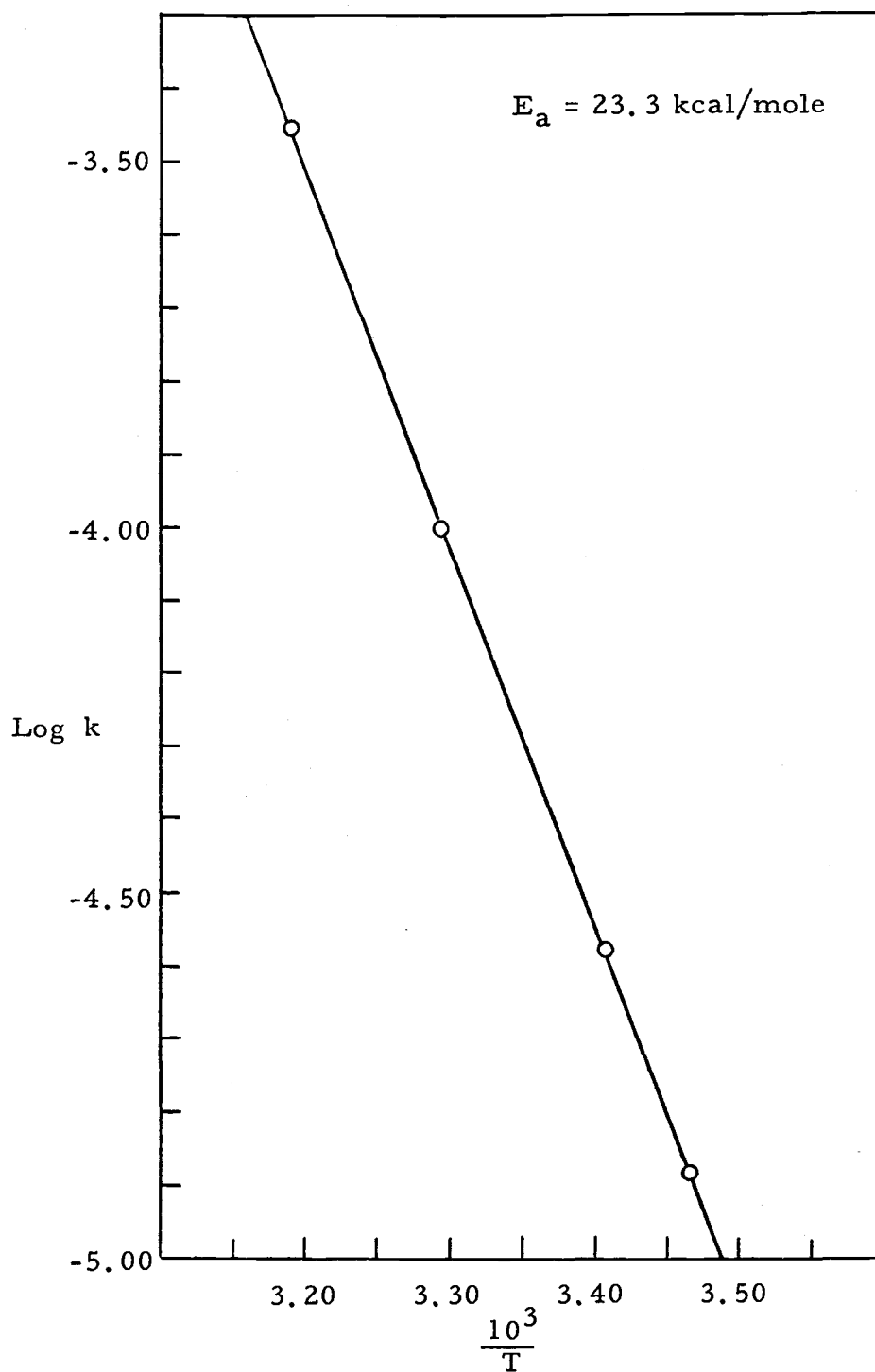
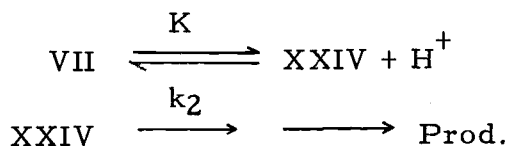


Figure 4. Arrhenius plot of the first-order rate constants for the ring closure of VII in presence of excess triethylamine in methanol.

behaviour, no drift in rates being observed (Figure 10).

The rate increase in presence of added base and the leveling-off effect suggest that XXIV is the actual form undergoing the ring closure. Thus apparently the function of the added base is simply to convert VII to XXIV which then reacts to give the observed products without further acid or base catalysis. Hence the reaction of VII in the media employed can be formulated as follows:



$$\text{Rate} = k_2 [\text{XXIV}]$$

Experimentally, the kinetics are measured in terms of  $[S]$  where:

$$[S] = [\text{XXIV}] + [\text{VII}]$$

now 
$$K = \frac{[\text{XXIV}][\text{H}^+]}{[\text{VII}]} = \frac{[\text{XXIV}][\text{H}^+]}{[S] - [\text{XXIV}]}$$

thus 
$$K[S] = K[\text{XXIV}] + [\text{H}^+][\text{XXIV}] = [\text{XXIV}](K + \text{H}^+)$$

$$[\text{XXIV}] = \frac{K[S]}{K + [\text{H}^+]} = \frac{[S]}{1 + \frac{[\text{H}^+]}{K}}$$

Therefore 
$$\text{Rate} = k_2 \frac{[S]}{1 + \frac{[\text{H}^+]}{K}}$$

1. In added base:

$$\frac{[H^+]}{K} \ll 1$$

$$\text{Rate} = k_2 [S]$$

2. In absence of added base:

$$\frac{[H^+]}{K} > 1$$

$$\text{Rate} \simeq k_2 K \frac{[S]}{[H^+]}$$

It is possible to test the rate law for case two above using the previously determined values for  $K$  and  $k_2$ .

$$\text{Rate} \simeq k_2 K \frac{[S]}{[H^+]} = k_{\text{obs}} [S]$$

$$k_{\text{obs}} = \frac{k_2 K}{[H^+]}$$

For  $[VII] = 5 \times 10^{-4} M$ ,  $[H^+] = 1.5 \times 10^{-5} M$ ;  $k_2 = 3.5 \times 10^{-4} \text{ sec}^{-1}$  at  $40^\circ C$  and  $K = 5 \times 10^{-7} M$  at  $25^\circ$

$$\text{calc'd } k_{\text{obs}} = \frac{(3.5 \times 10^{-4} \text{ sec}^{-1}) (5 \times 10^{-7} M)}{(1.5 \times 10^{-5} M)} \simeq 12 \times 10^{-6} \text{ sec}^{-1} \text{ at } 40^\circ$$

considering the approximations involved, the calculated value of  $k_{\text{obs}}$  compares reasonably with the observed value of  $6 \times 10^{-6} \text{ sec}^{-1}$  at  $40^\circ$ .

With the above rate law a possible explanation can be offered for the upward drift in  $k_{\text{obs}}$  (Figure 1). As the reaction

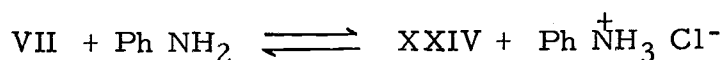


proceeds, the gradual consumption of  $[S]$  leads to a decrease in  $[XXIV]$  and  $[H^+]$ , and subsequent gradual increase in  $k_{obs}$ . A plausible explanation for the differences in kinetics shown in Figure 2 cannot be found as easily. The reaction at  $2 \times 10^{-5}$  M of VII (lower curve) starts off with a rapid initial rate which soon levels off and becomes the same as the rate for the "normal" reaction at  $5 \times 10^{-4}$  M (upper curve). The ratio of the rapid initial rate to the "normal" rate is not unlike that observed for the base catalysis by less-than-equimolar amounts of bases (Table I), and this suggests the possibility that the initial reaction is base catalyzed, and is brought about by minute amounts of impurities whose presence in methanol cannot generally be excluded. However, the fact that the initial catalyzed reaction soon reverts back to the uncatalyzed "normal" path requires that the basic impurities be consumed in the course of the reaction, a point for which a clear explanation cannot be provided.

With the previously presented scheme involving the intermediacy of the base form, it seemed appropriate to carry out the ring closure in media of constant ionic strength. This led to a study of the effect of added neutral salts such as lithium perchlorate on the ring closure of VII in methanol. The addition of a 100 fold excess of lithium perchlorate resulted in an

autocatalytic effect (Figure 5) where the upward drift in  $k_{\text{obs}}$  was even greater than previously observed. Because of this enhanced deviation from first-order behaviour, it was deemed necessary to forego the use of neutral salts in the interest of preserving the simplicity of the kinetics.

Despite all attempts, the reason for the above autocatalysis still remains unknown. At first glance the autocatalysis could be attributed to a secondary salt effect on the aniline that is produced in the reaction. Thus the addition of salts could conceivably help push the equilibrium below to the right. However, despite general



lack of precision, the equilibrium was found to be unaffected by addition of lithium perchlorate and/or aniline (Table VI). Furthermore, addition of lithium perchlorate has no effect on the rate of ring closure of XXIV (Table VII). Thus no experimentally verifiable explanation for the autocatalysis can as yet be offered.

#### Possible Mechanisms

In addition to being a triene, VII is an iminocarbonyl compound and might be expected to undergo reactions characteristic of carbonyl compounds. Thus it is possible to conceive of the

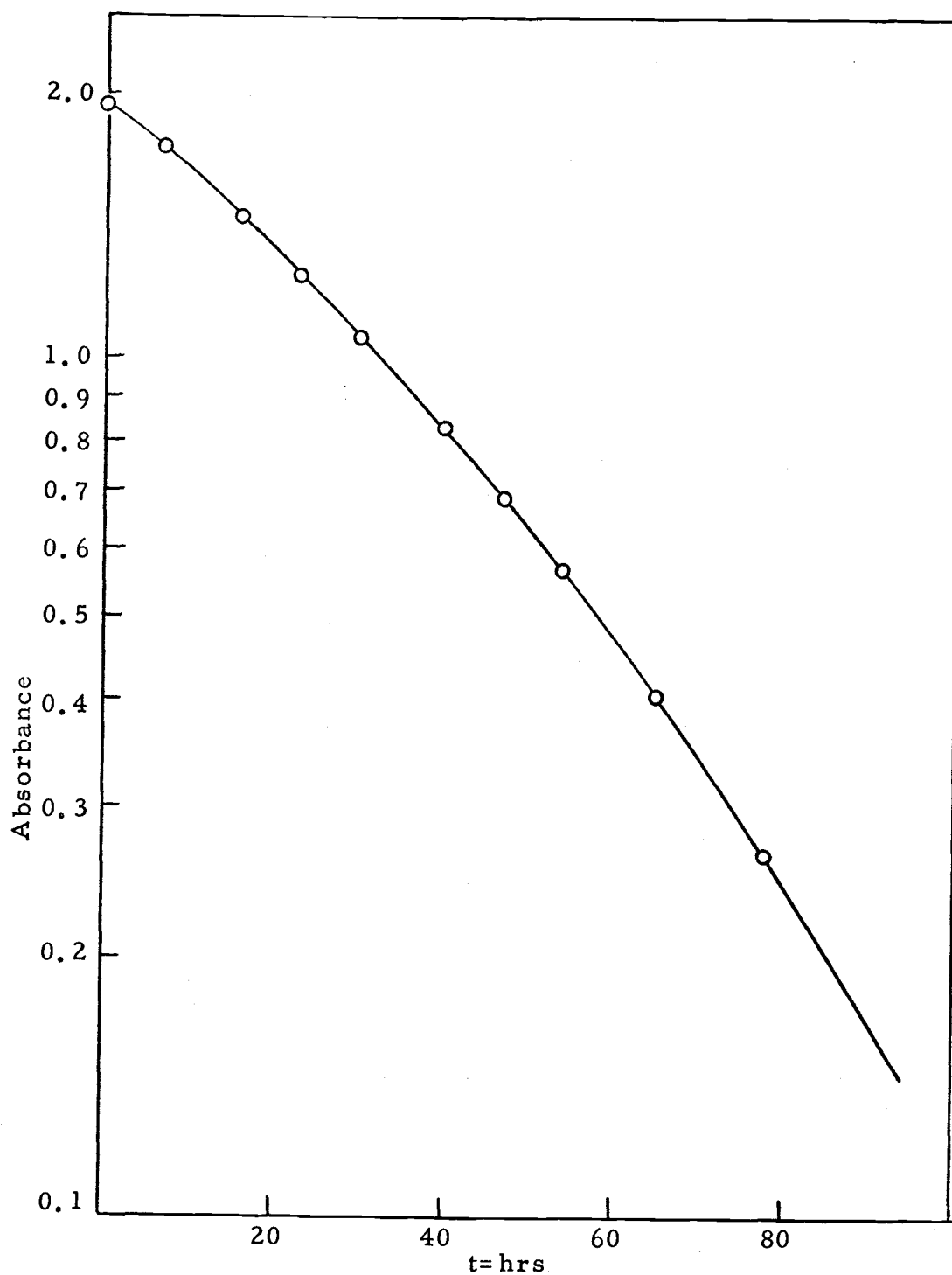
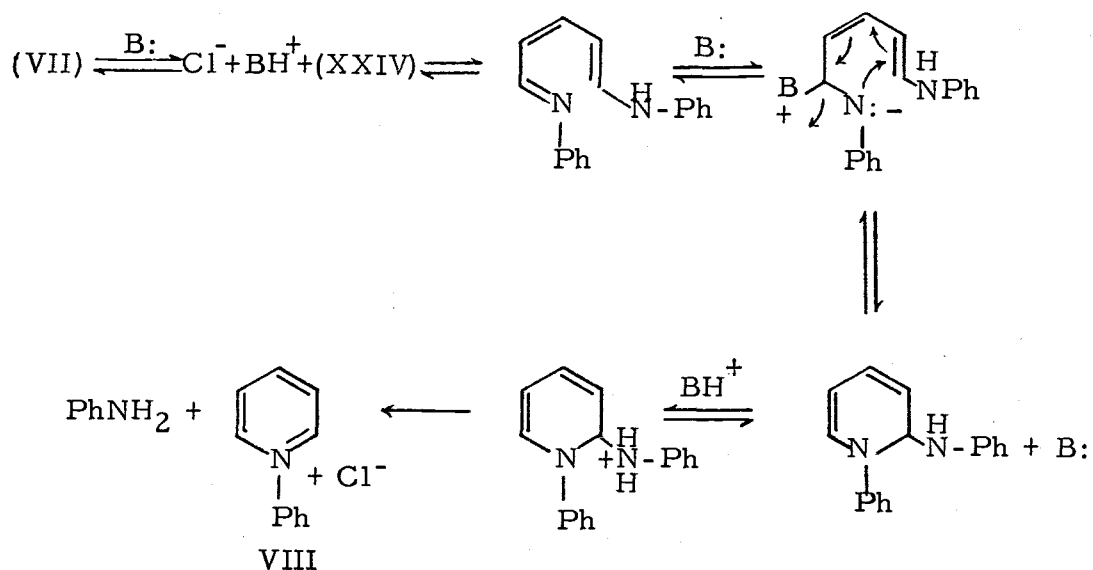


Figure 5. Plot of logarithm of absorbance vs. time for the ring closure of VII in methanol in presence of excess added  $\text{LiClO}_4$ .  $T = 40^\circ\text{C}$   $[\text{VII}] = 5 \times 10^{-4}$ ,  $[\text{LiClO}_4] = 5.0 \times 10^{-2}$ .



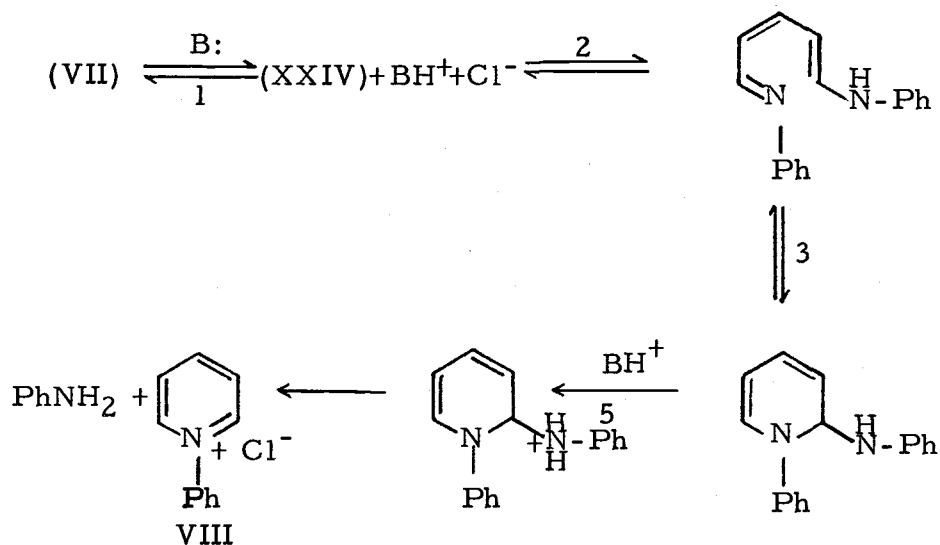
## Mechanism B



Mechanism A is an extension of the abnormal o-alkylation type aldol addition of carbonyl compounds (39, p. 480) where the nitrogen atom of the iminocarbonyl linkage of VII has taken part in the ring closure. Such an addition could occur through two separate but equivalent paths as shown. Mechanism B is an extension of the characteristic addition-elimination sequence for ester or amide hydrolysis (19, p. 291). With either of these mechanisms the rate of the reaction will be dependent on the nature of the base and its concentration. Thus both mechanisms can be dismissed as providing no explanation for the observed behaviour of VII in the presence of added bases.



## Mechanism D: Valence Isomerization



With either mechanism C or D, steps one and four are rapid proton transfers and step two may involve a proton transfer. Thus none of these steps would be expected to be rate-determining. Therefore, the rate-determining step must be either step three, or step five. The earlier-noted absence of dependence of the rate on the nature or concentration of the base when an excess of the base was present requires that if step five is rate-determining, then the reaction must be subject to general acid catalysis. In methanol solutions, methanol itself can act as the required acid and since its concentration is invariant, the catalysis would be undetectable.

To determine whether step five is rate-determining, the ring closure of VII was carried out in presence of excess triethylamine in methanol solutions containing different buffers of benzoic acid-sodium benzoate where the concentration of benzoic acid could be varied while its ratio to sodium benzoate concentration was held constant. These runs (Table VIII) carried out in constant and non-constant ionic strength and in the presence of up to 20 fold excess of benzoic acid (Figure 8) do not show any acid catalysis. Additionally, in order to eliminate the possibility of solvent involvement in some undetectable manner, similar acid catalysis studies were carried out in dry, neutral acetone (Table IX) with up to 200 fold excess of benzoic acid. Again no acid catalysis was observed. The absence of detectable general acid catalysis provides evidence against step five as the rate-determining step. Thus we shall assume step three to be rate-determining with either mechanism. In mechanism C this step involves ring closure by internal nucleophilic attack, while in mechanism D it involves ring closure by valence isomerization.

A choice between the above mechanisms can not easily be made. On the basis of the observed behaviour of the reaction, two objections can be raised to mechanism C. The ring closure by this mechanism bears close resemblance to the nucleophilic



addition of amines to carbonyl groups. However, the pH-rate profile of the latter reaction differs appreciably from the observed behaviour (Figure 3). The pH-rate profile for addition of hydroxylamine to acetone (21)

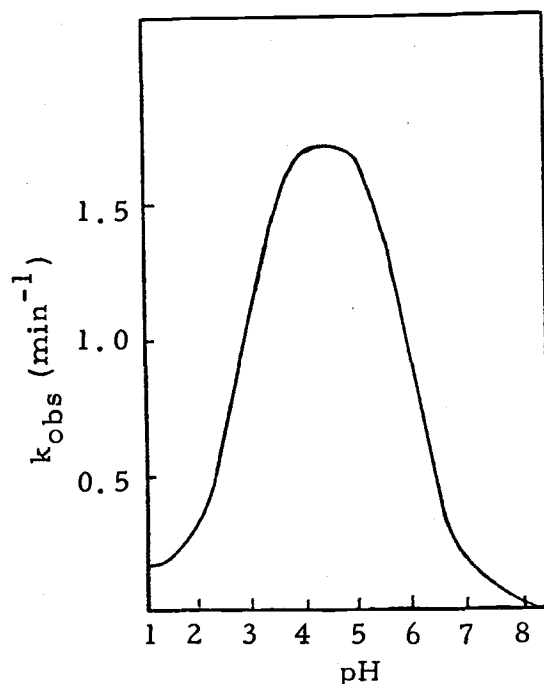
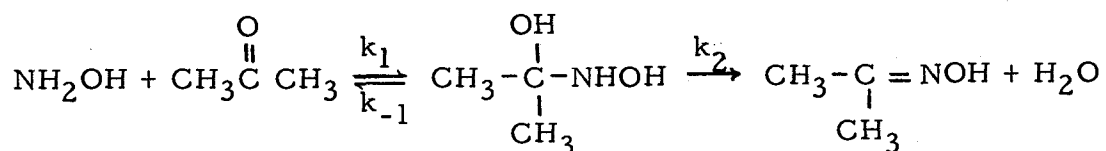
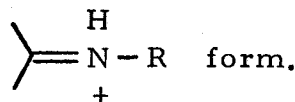


Figure 6. Effect of pH on the pseudo first-order rate constant for the reaction of  $5 \times 10^{-4}\text{M}$  acetone with  $1.67 \times 10^{-2}\text{M}$  total hydroxylamine (21).

exhibits a bell-shaped curve (Figure 6). This arises because of a change in the rate-determining step of the reaction. In basic pH the dehydration step is rate-determining and the rate is

accelerated as the pH is lowered to the near neutral range. However, further lowering of the pH to the acidic side brings about a decrease in rate due to a decrease in concentration of the free hydroxylamine, causing the addition step to become rate-determining. The behaviour of the ring closure reaction (Figure 3) is substantially different from the above in that although the rate is accelerated by the initial addition of base, a corresponding decrease in rate in presence of a large excess of base is not observed and the reaction is independent of the base concentration once all VII has been converted to XXIV.

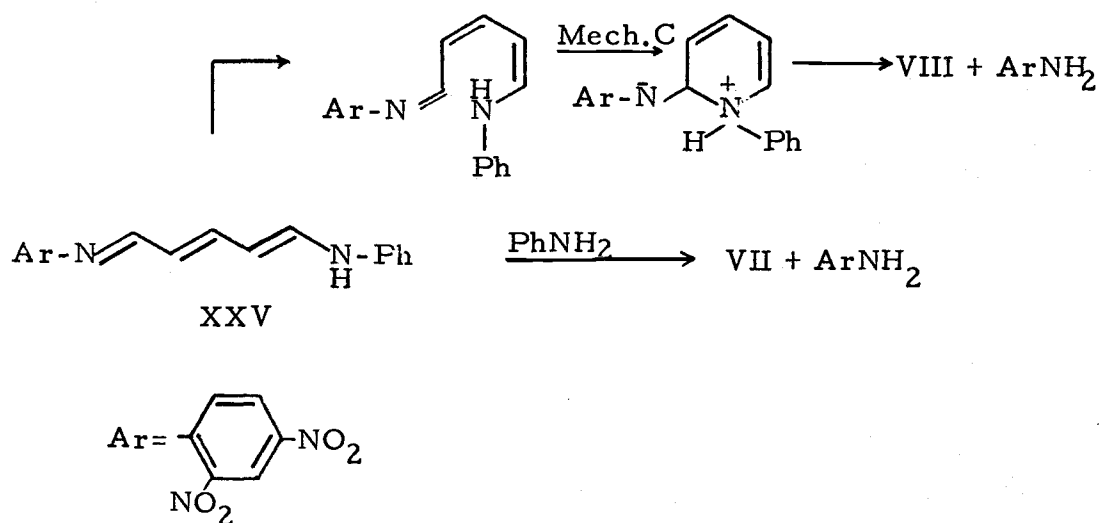
Additionally, ring closure by mechanism C proceeds through a rate-determining nucleophilic addition to an imine. It has generally been observed that such additions occur more readily when the imine is in the cationic



The cationic form is believed to be the reactive species in the addition of amines (6), water (45) and hydroxide ion (45) to imines and also in the Knoevenagel (7), Mannich (37) and the Vilsmeier (3) reaction. On this basis triene VII in which the imine linkage is protonated should be more reactive than its free base XXIV; a fact contrary to the experimental findings.

A second objection can be raised by considering the

reaction between 2,4-dinitrophenylpyridinium chloride (IX) and two moles of aniline that leads to the formation of VII. The addition of one mole of aniline to IX presumably leads to the intermediate XXV which might undergo further reaction by either of



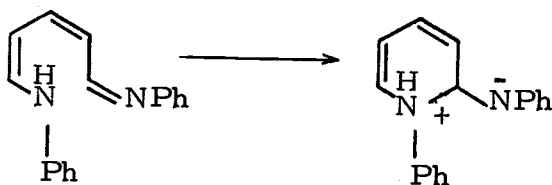
two pathways. If mechanism C is the correct mechanism, XXV would be expected to undergo ring closure to phenylpyridinium chloride (VIII) and 2,4-dinitroaniline. This internal nucleophilic addition should be particularly favorable since the dinitrophenyl group would stabilize the developing negative charge on the imino nitrogen. In competition with this unimolecular process is the bimolecular addition of aniline to the same iminocarbonyl. Though exhaustive studies have not been attempted, no evidence for the direct formation of phenylpyridinium chloride from XXV has been uncovered. Even in relatively dilute solution the

bimolecular reaction appears to proceed to the complete exclusion of the internal nucleophilic addition. Should XXV undergo valence isomerization process, it would of necessity give N-(2,4-dinitrophenyl)-2-anilino-1,2-dihydropyridine.

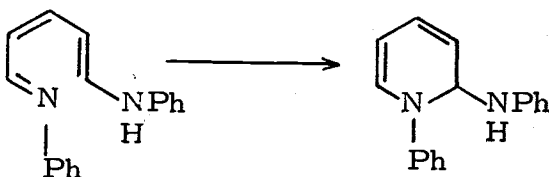
Although the objections discussed above to the adoption of mechanism C are reasonable, they are not sufficient for its summary dismissal. Thus additional experimental evidence seems needed before a final choice between the two mechanisms can be made.

With step three as the likely rate-determining step of the reaction with either mechanism, it is clear that mechanism C requires a transition state with considerable charge separation, while mechanism D leads to an uncharged transition state. One useful test to differentiate between the two mechanisms would be the effect of

Mechanism C



Mechanism D



solvent polarity on the reaction rate. Valence isomerization reactions are generally insensitive to solvent polarity due to their nonpolar transition state (38, p. 677). On the other hand high sensitivity is shown by reactions between nonpolar reactants which proceed through a dipolar transition state. The rates of these reactions show considerable acceleration with increasing dielectric constant of the solvent (44, p. 379-388). Thus if the ring closure of VII in presence of excess base proceeds by mechanism C, an appreciable decrease in rate would be expected in going from methanol, a solvent of high dielectric, to dioxane which has a low dielectric constant. No significant changes in rate would be expected by the above change if mechanism D was correct.

Consequently, the ring closure was carried out in a series of dioxane-methanol mixtures varying from pure methanol to 80% dioxane-20% methanol. The data, shown in Table X, indicates a small increase in rate with the increase in the amount of dioxane in solution, the rate constant increasing from  $9.6 \times 10^{-5} \text{ sec}^{-1}$  in methanol to  $4.60 \times 10^{-4} \text{ sec}^{-1}$  in 80% dioxane-20% methanol. A comparison of the ring closure rates in methanol, acetone and dioxane also shows (Table III) the same rate trend with the dielectric constants of the solvents. This trend, as discussed earlier, is contrary to the expected behaviour of a reaction proceeding

TABLE III. First-order rate constants for the ring closure of VII in methanol, acetone, and dioxane in presence of excess triethylamine.  $T = 30^{\circ}$

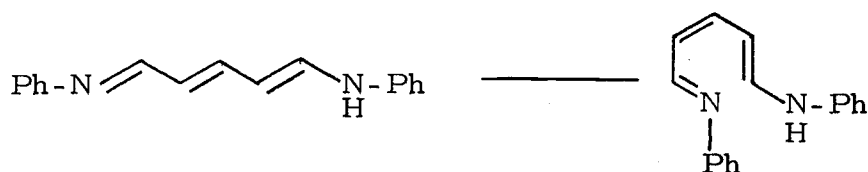
| $[\text{VII}] \times 10^5$<br>M | $[(\text{C}_2\text{H}_5)_3\text{N}] \times 10^4$<br>M | Solvent  | Dielectric constant <sup>a</sup><br>@25° | $k \times 10^4$<br>sec <sup>-1</sup> |
|---------------------------------|---|----------|--|--------------------------------------|
| 3.2                             | 6.0   | methanol | 32.6                                     | 0.96                                 |
| 3.1                             | 6.5   | acetone  | 20.7                                     | 5.8                                  |
| 10.0                            | 22.0  | dioxane  | 2.21                                     | 15.0(30)                             |

<sup>a</sup>Handbook of Chemistry and Physics, 48th Ed. The Chemical Rubber Co. 1967-1968.

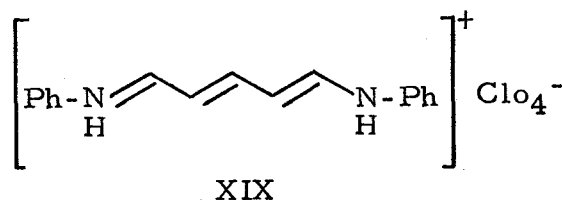
through a dipolar transition state. Although the above findings do not absolutely rule out other mechanisms, they are in better accord with a valence isomerization mechanism.

#### Changes in Configuration Attending Ring Closure

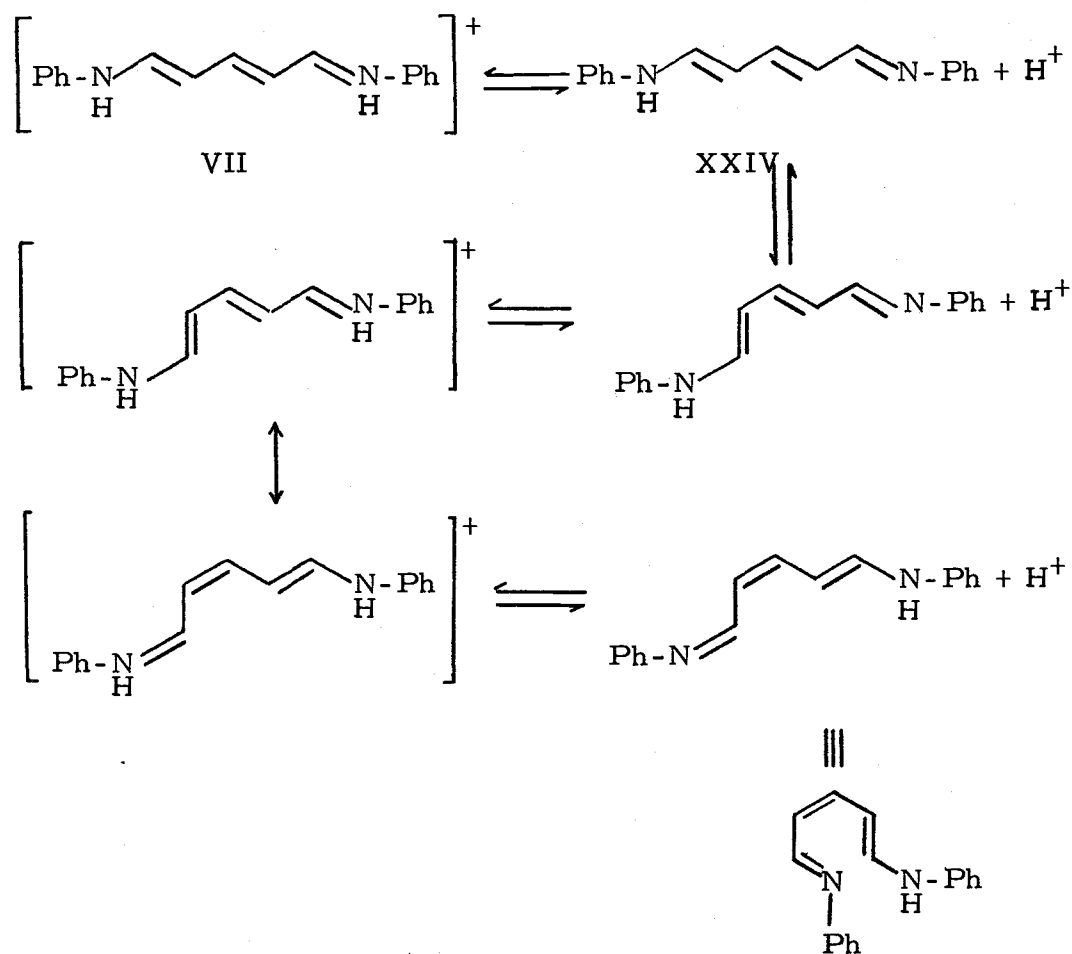
As was noted earlier, it is reasonable to assume that VII and XXIV will be in the all-trans configuration by analogy with the configuration established for XVIII (20). However, as the presentation of the valence isomerization mechanism shows (step two),



the ring closure process requires a cis configuration for the central double bond. The required cis-trans isomerization could be a simple thermal process since it has been shown (8) that the central double bond of triene XIX can be isomerized by irradiation with



visible light at its wavelength of maximum absorption. After irradiation the unstable cis isomer rapidly reverted to the all-trans form in the dark. However, in the media employed in this work, the facile equilibrium between XXIV and VII provides another possible route to isomerization via a series of protonation-deprotonation steps:



Since the facile thermal isomerization can occur only in the symmetrical resonance hybrid, a consequence of either scheme is that in the absence of a proton source, XXIV should be incapable of undergoing the isomerization. Thus a sample of XXIV dissolved in an aprotic solvent free from acid could not undergo ring closure.

To test the above hypothesis, XXIV was prepared by

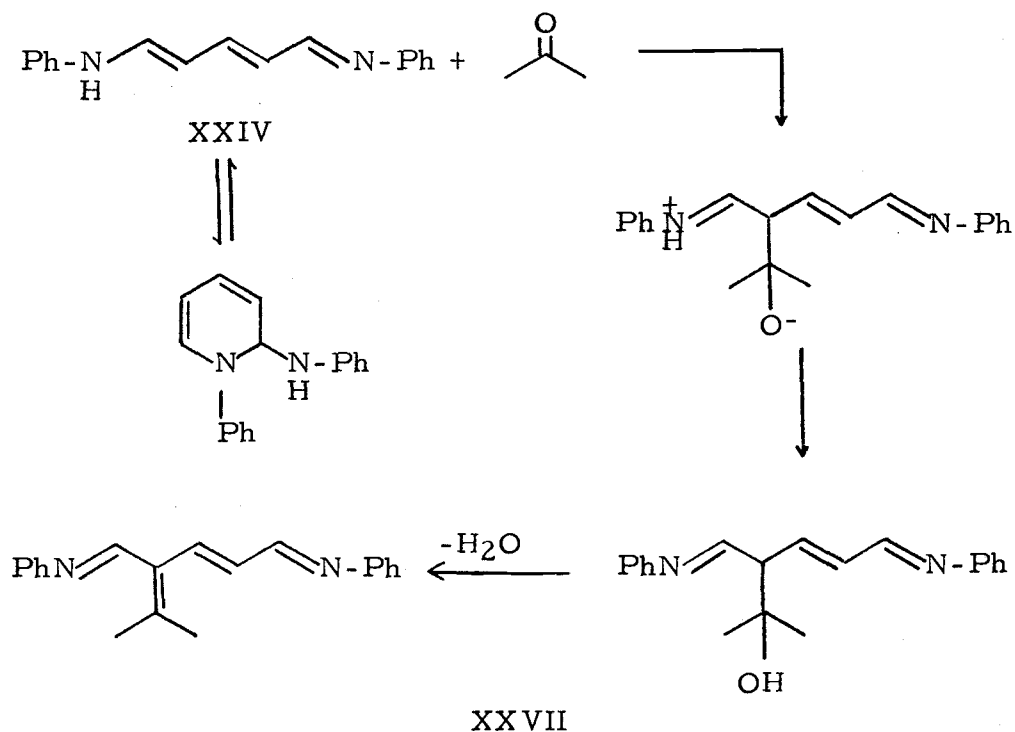


Zincke's method (47) through the treatment of VII in methanol with dilute aqueous sodium hydroxide. The isolated product, a yellow solid, had the melting point reported by Zincke, however, it was not possible to remove all of the solvent without causing decomposition of the compound. Moreover, it could not be purified by recrystallization from aprotic solvents. The absorption maximum of the compound in acetone at 388  $m\mu$  is the same as that observed for VII in the presence of base. At a concentration of  $4.3 \times 10^{-5}$  in carefully purified acetone under a nitrogen atmosphere the absorption band due to XXIV disappears with a first-order rate of  $3 \times 10^{-4} \text{ sec}^{-1}$  at  $30^\circ\text{C}$ . This value may be compared with the rate constant of  $5.8 \times 10^{-4} \text{ sec}^{-1}$  obtained for the ring closure of VII in acetone (Table III). Thus the free base XXIV does undergo the ring closure, but at a slightly reduced rate.

This result is not surprising since experimental difficulty in the complete removal of the solvent from XXIV left methanol or water of crystallization which could act as the proton source causing the isomerization of the double bond by the previously described scheme. Clearly a photochemical isomerization is possible as well, since the reaction was carried out in the spectrophotometer.

During these studies a curious behaviour of solutions of

XXIV in acetone was discovered. After the solutions were removed from the spectrophotometer at the termination of the kinetic studies, they reverted from colorless to yellow in a few hours. At the end of the kinetic studies the solutions did not show any absorption bands above  $340\text{ m}\mu$  (cut-off wavelength of acetone), but several hours after removal from the spectrophotometer they exhibited a broad band at  $410\text{ m}\mu$ . Control samples kept in the laboratory at room temperature lost the absorption band at  $388\text{ m}\mu$  and displayed a new one at  $410\text{ m}\mu$  upon standing for a few days. No attempt was made to isolate and identify the compound responsible for the  $410\text{ m}\mu$  peak; however, the above observations may possibly be accounted for by the scheme below:



The absorption maxima of XXVI should be similar to those of its parent compound N-phenyl-1,2-dihydropyridine which were found (40) to be 239 m $\mu$  ( $\epsilon$  8000) and 350 m $\mu$  ( $\epsilon$  12500) in ethanol.

Allowing for a hypsochromic shift in acetone similar to that ob-

served for XXIV ( $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  406 m $\mu$ ,  $\lambda_{\max}^{\text{CH}_3\text{COCH}_3}$  388 m $\mu$ ),

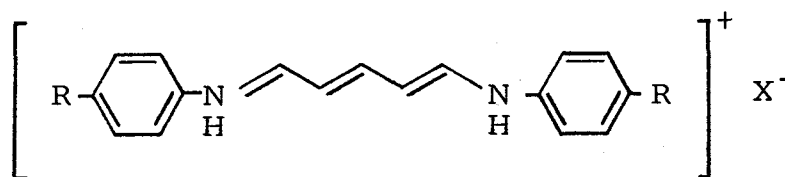
it appears likely that formation of XXVI would be spectrally undetectable in acetone, and only the subsequent formation of XXVII would be observed. The latter, owing to its cross-conjugated chromophore, could conceivably have its absorption maximum at 410 m $\mu$ .

Unfortunately the question of the role of the configurational changes in the ring closure process could not be unequivocally resolved by our studies owing to the experimental problems.

## Part Two

Synthesis and Kinetics of Ring Closure of Six Symmetrically Substituted Derivatives of VII

In order to determine the effect of substituents on rate, six



XXVIII

- a) R = CH<sub>3</sub>, X = Cl    d) R = F, X = Cl  
 b) R = OCH<sub>3</sub>, X = Cl    e) R = N(CH<sub>3</sub>)<sub>2</sub>, X = Cl  
 c) R = Cl, X = Cl    f) R = NO<sub>2</sub>, X = Br

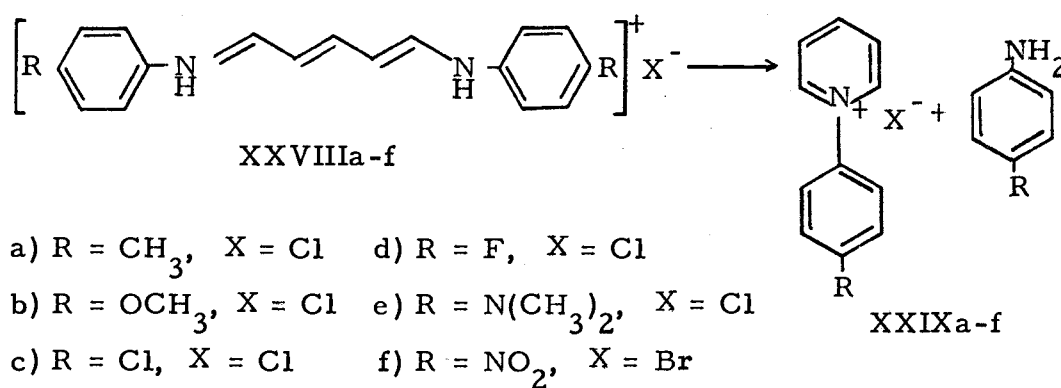
substituted derivatives of VII were prepared. Compound XXVIII a-e were prepared according to Zincke's procedure (47) by treating 2,4-dinitrophenylpyridinium chloride (IX) with the appropriate aromatic amine. Due to failure of the above method with p-nitroaniline, Konig's method (25) of treating cyanopyridinium bromide (XV) with p-nitroaniline was used. All compounds except XXVIII d are known, and were identified by melting point and spectral data. For XXVIII d a satisfactory carbon and hydrogen analysis was obtained.

As expected, the visible spectra of the trienes showed two peaks in the region between 550 and 400 m $\mu$ . These were assigned to the hydrochloride and the free base forms of the trienes respectively on the basis of values reported in the literature. For each substituted triene preliminary studies were made to ascertain whether the kinetics in presence of excess triethylamine were first-order, and independent of the amine concentration (Figures 9 and 10). Subsequently rate constants for ring closure of these compounds in methanol in presence of excess triethylamine were measured at three different temperatures (Table XI), and the activation parameters for the reactions were calculated. The data for XXVIIIa-f as well as VII are summarized in Table IV. Curiously, the ring closure of XXVIIIf in methanol alone is much faster than in presence of triethylamine, in contrast with the behaviour of other trienes.

TABLE IV. First-order rate constants and activation parameters for ring closure of trienes VII and XXVIIIa-f in methanol in presence of excess triethylamine.

| Comp'd  | R                                | $k \times 10^5 \text{ sec}^{-1}$ |      | $k \times 10^4 \text{ sec}^{-1}$<br>@40° | $\Delta H^\ddagger_{\pm 1} \text{ kcal}$<br>@30° | $\Delta S^\ddagger_{\pm 1}$<br>Cal/deg |
|---------|----------------------------------|----------------------------------|------|--|--|--|
|         |                                  | @20°                             | @30° |  |  |  |
| VII     | H                                | 2.65                             | 9.91 | 3.52                                     | 22.7   | 0.0                                    |
| XXVIIIa | CH <sub>3</sub>                  | 2.29                             | 8.46 | 3.11                                     | 22.8   | 0.2                                    |
| XXVIIIb | OCH <sub>3</sub>                 | 2.78                             | 10.5 | 3.65                                     | 22.3   | -1.3                                   |
| XXVIIIc | Cl                               | 4.75                             | 17.6 | 6.22                                     | 22.7   | 0.9                                    |
| XXVIId  | F                                | 4.31                             | 15.6 | 5.23                                     | 22.3   | -0.3                                   |
| XXVIIIe | N(CH <sub>3</sub> ) <sub>2</sub> | 2.00                             | 7.43 | 2.53                                     | 22.6   | -1.0                                   |
| XXVIIIf | NO <sub>2</sub>                  | 10.4                             | 36.4 | 12.0                                     | 21.7   | -0.8                                   |

For all these compounds except XXVIIIe the reaction was carried out on preparative scale under the conditions used for the kinetic studies. The products were shown to be the appropriate aromatic amine and the para-substituted phenylpyridinium halides (XXIX) in quantitative yield. Experimental difficulties prevented

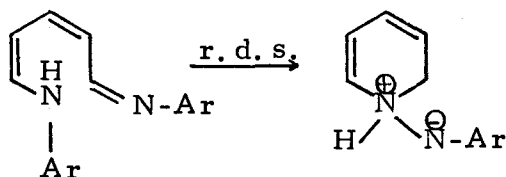


the identification of the products from the reaction of XXVIIIe, however, it has been reported (12) that in water XXIXe is formed.

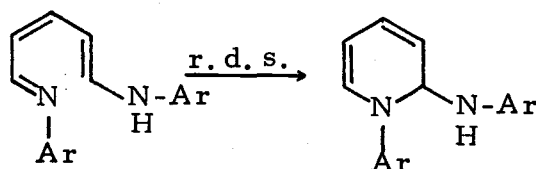
#### The Effect of the Substituents on the Reaction Rate

The effect of the para substituents on the rate of ring closure provides further data which may assist in distinguishing between mechanisms C and D. Here again due to the differences in polarity of the transition states of the two mechanisms, discernibly different results are expected. Since the same substituent is present on each

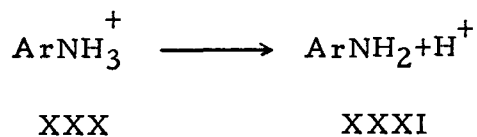
## Mechanism C



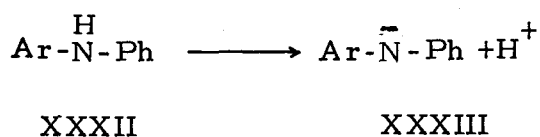
## Mechanism D



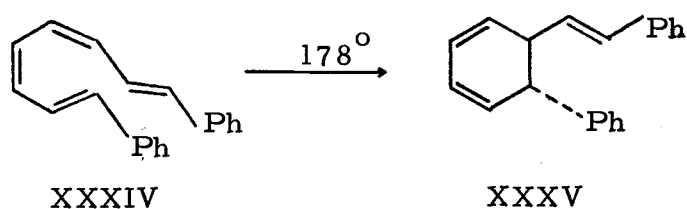
aryl group, they will be expected to show opposing effects on the rate if the reaction proceeds through mechanism C. However, the magnitude of these effects need not be equal. Indeed a comparison of model systems suggests that the two positions should exhibit measurably different susceptibilities to substituent effects. A Hammett plot (12, p. 184) for the dissociation of anilinium ions (XXX  $\rightarrow$  XXXI) shows a rho value of 2.89 (4), while on the other



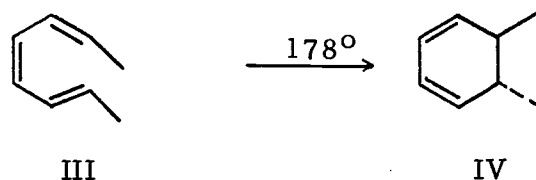
hand the rho value for the ionization of diphenylamines (XXXII  $\rightarrow$  XXXIII) was found to be 4.07 (9). Taking the difference between



the reactivities of these representative systems as an approximate measure, a rho of 1.2 is expected for mechanism C. As for the ring closure of trienes by valence isomerization, all available indications point to a lack of significant substituent effects. Thus the rate of the ring closure of XXXIV was found to be of the same

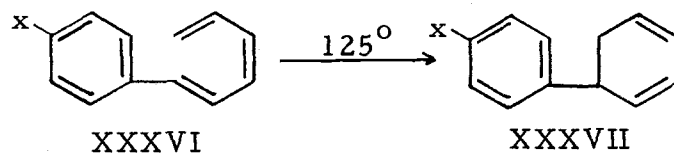


magnitude ( $6 \times 10^{-5} \text{ sec}^{-1}$ ) as the rate of  $2.2 \times 10^{-5} \text{ sec}^{-1}$  found for the ring closure of III at the same temperature (31). Similarly,



the ring closure of trienes XXXVIa and XXXVIb proceed at parallel rates of  $3.9$  and  $3.5 \times 10^{-5} \text{ sec}^{-1}$  respectively (33).





a)  $x = H$

b)  $x = Cl$

Examination of the data in Table IV shows that the rate of ring closure is remarkably insensitive to the substituents. Thus within experimental error all seven compounds show  $\Delta H^\ddagger = 22.4$  kcal/mole and  $\Delta S^\ddagger = 0, 0 \text{ Cal. deg}^{-1} \cdot \text{mole}^{-1}$ . Although the rate data do not fit a Hammett (18, p. 184) plot, for the sake of comparison a rho value of roughly 0.3 can be obtained by drawing a reasonable line through the points in Figure 7. This rho value falls much short of the rho value of 1.2 expected for mechanism C, and examination of the relative rate constants expected with the latter rho with the observed relative rates (Table V) reveals another significant difference. Whereas the electron donating substituents were expected to cause a pronounced deceleration of the rate, they show almost no effect on the observed rates.

The electron withdrawing substituents do, however, cause a slight increase in rate. Although their effects are quite small, they are nonetheless in the same direction as that of the expected

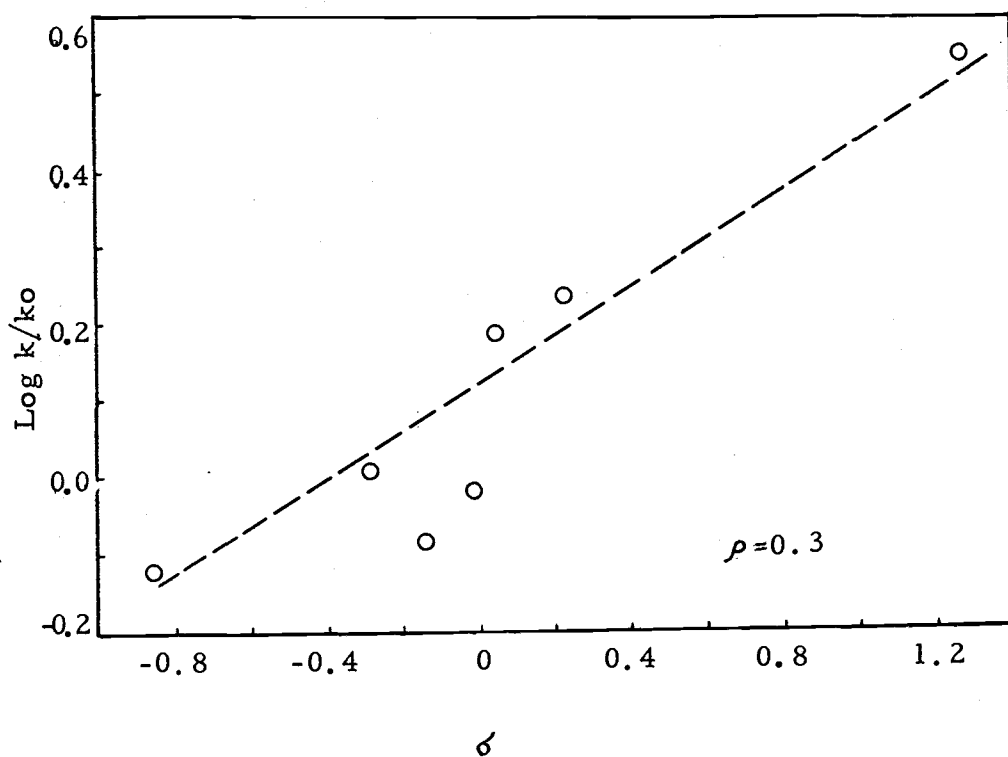


Figure 7. Hammett type plot of the first-order rate constants of XXVIIIa-f at 30°C.

TABLE V. Comparison of the observed relative rate with relative rate expected for  $\rho = 1.2$ .

| Substituent                      | $k/k_0$ (obs) | $k/k_0$ ( $\rho = 1.2$ ) |
|----------------------------------|---------------|--------------------------|
| N(CH <sub>3</sub> ) <sub>2</sub> | 0.75          | 0.10                     |
| OCH <sub>3</sub>                 | 1.06          | 0.47                     |
| CH <sub>3</sub>                  | 0.85          | 0.63                     |
| F                                | 1.55          | 1.18                     |
| Cl                               | 1.70          | 1.88                     |
| NO <sub>2</sub>                  | 3.70          | 33.4                     |

effects (Table V). This somewhat diminishes the effectiveness of the data as an aid in distinguishing between the mechanisms.

However, although other mechanisms can not be excluded, in view of the previously presented experimental evidence and the theoretical considerations, the above data are better accommodated by a valence isomerization mechanism than any alternate mode of reaction.

## CONCLUSIONS

A kinetic study of the ring closure of a series of diazaheptatrienes has provided evidence indicating that the rate-determining step is a valence isomerization process. Preparative scale studies confirmed that these ring closures are clear cut processes free from any measurable side reactions. The series of substituted diazatrienes showed remarkable insensitivity in rate and in activation parameters to changes in para-substituents. Reactivity of the azatriene electrocyclization falls between those of the cis-hexatrienes and the cis-dienones. In terms of the enthalpies of activation the cis-hexatrienes fall near 28 kcal/mole, the present cases near 23 and the dienones around 20 kcal/mole. Thus the resemblance is closer between azatriene and dienone than between azatriene and hexatriene. The causes of these differences are as yet unknown.

## EXPERIMENTAL

A Cary 15 spectrophotometer was used to determine all ultraviolet and visible spectra. The infrared spectra were recorded on a Beckman IR 8 instrument. Melting points were determined by the capillary method in a liquid bath and are corrected.

1,7-Diphenyl-1,7-diaza-1,3,5-heptatriene(VII)

This compound was prepared according to the procedure given by Zincke (47). A solution of 8.00 g (86 m moles) of aniline in 100 ml of 80% aqueous ethanol was slowly added to a solution of 12.09 g (39 m moles) of 2,4-dinitrophenylpyridinium chloride (IX) (47) in 100 ml of the same solvent. Immediately upon addition an intense red color developed in the solution, and after several minutes crystals of VII began to appear. At intervals of ten to fifteen minutes the crystals were removed by filtration until formation of crystals of 2,4-dinitroaniline on the vessel walls were noted, at which time the solution was discarded. The product was recrystallized from methanol, washed with ether, and dried under vacuum to constant weight m. p. 146-147°,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  485 m $\mu$  ( $\epsilon$  115000). (lit. m. p. 142-143° (47),  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  485 m $\mu$  ( $\epsilon$  127000) (14)).

### Kinetic Studies

Kinetic runs at low concentrations ( $\sim 10^{-5}$  M) where the triene employed was mostly ( $> 95\%$ ) in a single form were carried out inside the thermostated cell compartment of the Cary 15 spectrophotometer. The temperature inside the cell was maintained within  $\pm 0.1^\circ\text{C}$ . Stock solutions of the triene employed and any other added compound were diluted to the proper concentration and their temperature was brought to within a few degrees of the specified temperature in a water bath. After mixing, the solutions were placed in the cell compartment and allowed to come to thermal equilibrium for two to three minutes. The rates were measured by following the changes in the absorbance of the triene.

Kinetic runs at high concentration ( $5 \times 10^{-4}$  M) of VII or where VII and XXIV were both present to considerable extent in solution were carried out in a constant temperature oil bath capable of maintaining the temperature to  $\pm 0.2^\circ$ . Stock solutions of VII and any other added compound were prepared and diluted to the proper concentration. After their temperature was brought up to within a few degrees of the bath temperature, the solutions were mixed and placed in a kinetic vessel inside the oil bath. The reaction vessel was equipped with a condenser and a discharge

nozzle and was maintained under a nitrogen atmosphere. At appropriate intervals aliquotes were forced out with nitrogen pressure and quenched with hydrochloric acid to convert all XXIV present to VII. After dilution, the concentration of VII in the samples were determined spectrophotometrically.

All kinetic runs were allowed to proceed to at least 75% completion. The rate constants were determined by plotting  $\log (A - A_{\infty}) / (A_0 - A_{\infty})$  vs. time (11. p. 12) for the absorbance of the triene employed. Clean first-order kinetics were observed for all ring closures in presence of excess added base, examples of which are shown in Figures 8, 9 and 10. Drift in rates were observed for the ring closure of VII in methanol, for which average rate constants were computed. Drifts were also observed in kinetic runs employing 1/5 equivalent of added base (Table II, runs 1, 4 and 8). Due to constant changes in the ratio of base to substrate concentration, initial rate constants were reported for these runs.

#### Equilibrium Studies

Stock solutions of aniline and/or lithium perchlorate in methanol were properly diluted and placed in a water bath near 25°C. Fresh solutions of VII in methanol at 25°C were quickly diluted, mixed with aniline and/or lithium perchlorate solutions

and placed immediately in the Cary 15 spectrophotometer, the cell compartment of which was also thermostated at 25°C. The complete spectrum of the compound was immediately scanned, followed by addition of a microdrop of hydrochloric acid to the cell solution, after which a second scan was made. Thus the equilibrium concentration of VII as well as the combined concentrations of VII and XXIV were determined, from which the  $K_{eq}$  was computed.

The methanol employed in these studies was assumed to contain no other acids or bases, since attempts at determination of the amounts of extraneous acids or bases present were unsuccessful. The possibility of employing neutral red (23) ( $pK_a = 8.2$ ) as an indicator was explored, but this indicator exists principally in its acid form in methanol and its absorption peaks (532 and 460  $m\mu$ ) interfere with those of the substrate.

#### Phenylpyridinium Chloride (VIII)

To 1.40 g (4.9 m moles) of VII in 500 ml of 80% dioxane-20% methanol was added 2.69 g (26.6 m moles) of triethylamine, and the solution was kept at 25°C for 18 hours. After evaporation of the solvent, repeated washing of the residue with ether removed the aniline, and left 1.05 g (110%) of solid phenylpyridinium



chloride (VIII) which was recrystallized from ethanol-ethylacetate solution to give white needles, m.p.  $104^{\circ}$ , in agreement with the reported value of  $105^{\circ}$  (47). The aniline isolated from the ether wash weighed 0.43 g (93%) and had IR and U. V. spectra identical to an authentic sample. The melting point of its benzamide derivative was  $163^{\circ}$  (lit. (42, p. 288)  $160^{\circ}$ ).

Free base of 1,7-diphenyl-1,7-diaza-1,3,5-heptatriene (XXIV)

This compound was prepared according to the procedure given by Zincke (47). Dilute sodium hydroxide solution was slowly added to a solution of VII in methanol. The initial red color gradually turned to bright yellow, with crystals of XXIV appearing in the solution. The addition was discontinued when no further changes in color were observed. The crystals were removed by filtration, and were air dried for 24 hours followed by further drying in an evacuated desiccator for another 24 hours; m.p.  $84-85^{\circ}$ ,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  407  $m\mu$  ( $\epsilon$  67000),  $\lambda_{\max}^{\text{CH}_3\text{COCH}_3}$  388  $m\mu$ . (lit. (15), m.p.  $85-86^{\circ}$ ,  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  406  $m\mu$  ( $\epsilon$  65000)).

Preparation of Substituted Trienes (XXVIIIa-f)

General Procedure: XXVIIIa-e were prepared by the method of Zincke (47), through the reaction of the appropriate aromatic amine with 2,4-dinitrophenylpyridinium chloride (IX).

Details of the preparation are the same as outlined for the unsubstituted triene VII. Because of the failure of the above reaction with p-nitroaniline, Konig's method (25) was adopted for synthesis of XXVIII<sub>f</sub>.

Trienes XXVIII<sub>a-c</sub>, <sub>e</sub>, <sub>f</sub> are known and were identified by comparison of their melting points and absorption maxima as well as those of their free bases with the values reported in the literature. As has been previously noted (12, 43), the melting points of these trienes appear to be somewhat dependent on the solvent of crystallization and also on how well they have been dried. The melting points reported here are for the samples dried to a constant weight under vacuum. The extinction coefficients of the trienes XXVIII<sub>a-f</sub> were determined in presence of several fold excess of hydrochloric acid or aniline hydrochloride in methanol. An excess of triethylamine was used for the extinction coefficients of their base forms.

1, 7-Di-(p-methylphenyl)-1, 7-diaza-1, 3, 5-heptatriene(XXVIII<sub>a</sub>)

To a solution of 2.97 g (10 m moles) of IX in 25 ml of 80% aqueous ethanol was slowly added 1.11g (10 m moles) of p-toluidine. Work-up in the previously described manner followed by recrystallization from methanol provided violet needles, m. p.

134-135°. which after drying melted at 153-154°;  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  485 m $\mu$   
 ( $\epsilon$  100000) (lit. m. p. 142-143° (47)  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  495 m $\mu$   
 ( $\epsilon$  99000) (14)). In presence of excess triethylamine, XXVIIIa  
 was converted to its free base,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  400 m $\mu$  ( $\epsilon$  35000) (lit.  
 $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  412 m $\mu$  ( $\epsilon$  35000) (15)).

1,7-Di-(p-methoxyphenyl)-1,7-diaza-1,3,5-heptatriene(XXVIIIb)

Treatment of 10.59 g (38 m moles) of IX in 75 ml of 80%  
 aqueous ethanol with 4.69 g (38 m moles) of p-anisidine, followed  
 by the usual purification and drying gave dark-red needles of  
 XXVIIIb, m. p. 150-151°,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  497 m $\mu$  ( $\epsilon$  94000). The re-  
 ported data are: m. p. 168-170° (from acetone-ethanol) 127-129°  
 (from ethanol) (43),  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  500 m $\mu$  ( $\epsilon$  82000) (14). The free  
 base,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  414 m $\mu$  ( $\epsilon$  63000), was obtained by addition of  
 triethylamine. The reported data for the free base are:  
 $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  415 m $\mu$  ( $\epsilon$  39000) (15).

1,7-Di-(p-chlorophenyl)-1,7-diaza-1,3,5-heptatriene(XXVIIIc)

Ten grams (32 m moles) of IX and 3.62 g (28 m moles) of  
 p-chloroaniline were allowed to react in 75 ml of 80% aqueous  
 ethanol. The isolated XXVIIIc was recrystallized from methanol  
 and dried, affording red needles, m. p. 139°,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  492 m $\mu$

( $\epsilon$  112000) (lit. m. p. 143° (47),  $\lambda_{\max}$  494 m $\mu$  (43)).

Treating XXVIIIc with triethylamine resulted in its conversion to the free base,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  410 m $\mu$  ( $\epsilon$  67000).

1,7-Di-(*p*-fluorophenyl)-1,7-diaza-1,3,5-heptatriene(XXVIII d)

*p*-fluoroaniline (16.43 g, 148 m moles) was slowly added to a solution of 20.78 g (67 m moles) of IX in 100 ml of 80% aqueous ethanol. The pure, dry crystals of XXVIII d, obtained in the usual manner, were bright red; m. p. 128-129°,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  478 m $\mu$  ( $\epsilon$  100,000).

Anal. calc'd for C<sub>17</sub>H<sub>15</sub>ClF<sub>2</sub>N<sub>2</sub>: C, 63.66; H, 4.72.

Found: C, 63.45; H, 4.86.

In the presence of excess added triethylamine XXVIII d was converted to its free base,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  403 m $\mu$  ( $\epsilon$  60000).

1,7-Di-(*p*-N,N-dimethylaminophenyl)-1,7-diaza-1,3,5-heptatriene (XXVIII e)

To 13.3 g (43 m moles) of IX in 300 ml of 80% aqueous ethanol was added 12.3 g (90 m moles) of N,N-dimethyl-*p*-phenylenediamine. The product was recrystallized from methanol and dried, affording purple needles, m. p. 141°,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  548 m $\mu$  ( $\epsilon$  82000) (lit. m. p. 147° (12),  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  550 m $\mu$  ( $\epsilon$  93000))

(14)). The free base form had a single sharp maximum at 440 m $\mu$  ( $\epsilon$  62000) in methanol. The reported data are:  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  440 m $\mu$  ( $\epsilon$  34000) (15).

1,7-Di-(p-nitrophenyl)-1,7-diaza-1,3,5-heptatriene (XXVIII f)

This compound was prepared according to the procedure given by Konig (25). To a solution of 4 ml (50 m moles) of pyridine in 50 ml of 95% ethanol was cautiously added 5.3 g (50 m moles) of solid cyanogen bromide. The resulting yellow solution was slowly added with stirring to a solution of 14 g (100 m moles) of p-nitroaniline in 200 ml of 95% ethanol at 50<sup>0</sup>. Immediately upon addition an intense red color developed in the solution and after several minutes crystals of XXVIII f began to appear. The crystals were removed by filtration at ten minute intervals and immediately air dried. After the fourth crop of crystals was collected, the solution was discarded. The combined product was washed with two litres of ether and dried under vacuum to a constant weight; m. p. 171-172<sup>0</sup>,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  522 m $\mu$  (lit. m. p. 149<sup>0</sup> (25),  $\lambda_{\max}^{524}$  m $\mu$ (43)). Due to rapid ring closure, it was not possible to measure the extinction coefficient. By treating with triethylamine, XXVIII f was converted to its free base,  $\lambda_{\max}^{\text{CH}_3\text{OH}}$  452 m $\mu$  ( $\epsilon$  54000) (lit. (15)  $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$  445 m $\mu$  ).

### Product Studies

General Procedure: the triene was dissolved in methanol containing excess triethylamine and was heated at the specified temperature until all of the triene had reacted. The solvent was evaporated and the residue was washed repeatedly with ether to separate the aromatic amine produced in the reactions. The isolated amines were identified by comparison of the U. V. and IR spectra with those of authentic samples. The p-substituted phenylpyridinium halides left from the ether wash were recrystallized from ethanol-ethyl acetate and identified by comparison of their melting points or those of their derivatives with the reported values. Satisfactory carbon and hydrogen analyses were obtained for the previously unknown XXIXa, d.

#### (p-Methylphenyl)pyridinium chloride (XXIXa)

On gram (3.2 m moles) of XXVIIIa and 1.62 g (16 m moles) of triethylamine were dissolved in 300 ml of methanol and heated for eight hours at 50°. After evaporation of the solvent 0.31 g (90%) of p-toluidine and 0.685 g (104%) of XXIXa were isolated from the residue. The recrystallized XXIXa, m.p. 206°, was converted by Konig's method (25) to its ferric chloride derivative,

m. p. 156-157°.

Anal. calc'd for  $C_{12}H_{12}Cl_4FeN$ : C, 39.18; H, 3.29

Found: C, 39.04; H, 3.31.

(p-Methoxyphenyl) pyridinium chloride (XXIXb)

To 1.04 g (3.0 m moles) of XXVIIIb in 200 ml of methanol was added 1.56 g (15.5 m moles) of triethylamine and the resulting solution was heated at 65° for 24 hours. Work-up by the previously described procedure afforded p-anisidine, 0.33 g (88%), and XXIXb, 0.71 g (105%), m. p. 133° (from ethanol-ethyl acetate) (lit. (47) m. p. 137°).

(p-Chlorophenyl)pyridinium chloride (XXIXc)

One gram (2.8 m moles) of XXVIIIc was dissolved in 300 ml of methanol and treated with 1.97 g (19 m moles) of triethylamine. After heating for 24 hours at 55°, the solvent was evaporated and the residue was washed with ether to yield 0.22 g (60%) of p-chloroaniline. The remaining residue consisted of 0.76 g (119%) of XXIXc which was purified by recrystallization; m. p. 127-128° (lit. (47) m. p. 123-124°).

(p-Fluorophenyl)pyridinium chloride (XXIXd)

A solution of 2.00 g (6.2 m moles) of XXVIIIId and 3.01 g (30 m moles) of triethylamine was kept at 60° for 12 hours. By the usual procedure 0.65 g (93%) of p-fluoroaniline and 1.35 g (103%) of XXIXd were isolated as the products of the ring closure. A ferric chloride derivative of XXIXd was prepared according to Konig's procedure (25); m. p. 168°.

Anal. calc'd for C<sub>11</sub>H<sub>9</sub>Cl<sub>4</sub>F FeN: C, 35.53; H, 2.44.

Found: C, 35.36; H, 2.33.

(p-Nitrophenyl)pyridinium bromide (XXIXf)

To 0.20 g (0.48 m moles) of XXVIIIIf in three litres of methanol was added 5.0 g (49 m moles) of triethylamine and the resulting solution was kept at 30°C. After 16 hours the solvent was evaporated, and 59 mg (91%) of p-nitroaniline was isolated from the residue by repeated washing with ether. The remaining solid XXIXf (144 mg, 106%) was converted to its ferric chloride derivative; m. p. 146-147° (lit. (25) m. p. 149°).



TABLE VI. Effect of added lithium perchlorate and aniline on the equilibrium between VII and XXIV in methanol, at 25°.

| $[\text{VII}] \times 10^5$<br>M (initial conc.) | $[\text{Aniline}] \times 10^5$<br>M | $[\text{LiClO}_4] \times 10^3$ | $K_{\text{eq}} \times 10^7$ |
|---|-------------------------------------|--------------------------------|-----------------------------|
| 1.0   | ---                                 | ---                            | 5                           |
| 1.0   | 0.1                                 | ---                            | 5                           |
| 1.0   | 0.5                                 | ---                            | 5                           |
| 1.0   | 1.0                                 | ---                            | 6                           |
| 0.94  | 1.0                                 | 1.0                            | 7                           |

TABLE VII. Effect of added lithium perchlorate on the first-order rate constant for ring closure of (VII) in methanol in presence of excess triethylamine. T = 40°C.

| $[\text{VII}]_{\text{M}} \times 10^5$ | $[(\text{C}_2\text{H}_5)_3\text{N}]_{\text{M}} \times 10^3$ | $[\text{LiCO}_4]_{\text{M}} \times 10^3$ | $k \times 10^4$<br>sec <sup>-1</sup> |
|---------------------------------------|---|--|--------------------------------------|
| 1.99                                  | 1.00  | ---                                      | 3.48                                 |
| 1.99                                  | 1.00  | 2.00                                     | 3.53                                 |

TABLE VIII. First-order rate constants for ring closure of (VII) in buffered methanol solutions at 39.2°.  $[\text{VII}] = 2.13 \times 10^{-5} \text{M}$ ,  $[(\text{C}_2\text{H}_5)_3\text{N}] = 2.21 \times 10^{-4} \text{M}$  (solvent, methanol - 1%  $\text{H}_2\text{O}$ )

| $[\text{benzoic acid}]$ ,<br>$\times 10^5 \text{ M}$ | $[\text{sodium benzoate}]$ ,<br>$\times 10^4 \text{ M}$ | $[\text{LiClO}_4]$ ,<br>$\times 10^4 \text{ M}$ | $k \times 10^4$<br>$\text{sec}^{-1}$ |
|--|---|---|--------------------------------------|
| ---  | ---   | ---   | 2.73                                 |
| 0.11   | 0.10  | ---   | 2.72                                 |
| 0.21   | 0.20  | ---   | 2.73                                 |
| 1.06   | 1.01  | ---   | 2.81                                 |
| 1.60   | 1.52  | ---   | 2.75                                 |
| 2.13   | 2.03  | ---   | 2.73                                 |
| ---  | ---   | 2.03  | 2.75                                 |
| 0.11   | 0.10  | 1.93  | 2.74                                 |
| 0.21   | 0.20  | 1.83  | 2.72                                 |
| 1.06   | 1.01  | 1.01  | 2.78                                 |
| 1.60   | 1.52  | 0.51  | 2.77                                 |
| 4.04   | 4.00  | 36.0  | 2.80                                 |
| 10.1   | 10.0  | 30.0  | 2.89                                 |
| 20.2   | 20.0  | 20.0  | 2.98                                 |
| 30.3   | 30.0  | 10.0  | 3.10                                 |
| 40.4   | 40.0  | ---   | 3.12                                 |

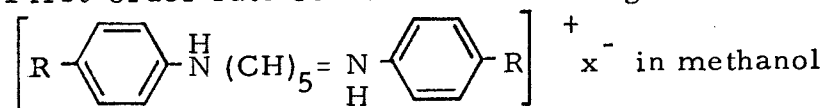
TABLE IX. First-order rate constants for the ring closure of (VII) in acetone at 30°. [VII] =  $3.1 \times 10^{-5}$  M.  $[(C_2H_5)_3N] = 6.5 \times 10^{-4}$  M.

| [benzoic acid]<br>$\times 10^4$ M | $k \times 10^4$<br>sec <sup>-1</sup> |
|-----------------------------------|--------------------------------------|
| ---                               | 5.79                                 |
| 0.31                              | 6.19                                 |
| 0.61                              | 6.32                                 |
| 0.92                              | 6.40                                 |
| 3.07                              | 6.37                                 |
| 6.14                              | 6.35                                 |
| 12.3                              | 6.39                                 |
| 30.7                              | 6.42                                 |
| 46.1                              | 6.40                                 |
| 61.4                              | 6.45                                 |

TABLE X. First-order rate constants for the ring closure of (VII) in methanol-dioxane solutions at 30°C. [VII] =  $3.24 \times 10^{-4}$  M.  $[(C_2H_5)_3N] = 5.15 \times 10^{-4}$  M

| dioxane<br>% v | $k \times 10^4$<br>sec <sup>-1</sup> |
|----------------|--------------------------------------|
| 0.0            | 0.96                                 |
| 4.0            | 1.01                                 |
| 8.0            | 1.08                                 |
| 20.0           | 1.26                                 |
| 40.0           | 1.72                                 |
| 60.0           | 2.56                                 |
| 80.0           | 4.60                                 |

TABLE XI. First-order rate constants for the ring closure of



in presence of triethylamine.

| T<br>°C | R                                | x  | [triene] x 10 <sup>5</sup> | [(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N] x 10 <sup>4</sup> | k x 10 <sup>5</sup> |
|---------|----------------------------------|----|----------------------------|---|---------------------|
|         |                                  |    | M                          | M   | sec <sup>-1</sup>   |
| 15.0    | H                                | Cl | 1.80                       | 3.85  | 1.32                |
| 20.0    | "                                | "  | 1.90                       | 6.88  | 2.65                |
| 30.0    | "                                | "  | 2.14                       | 4.89  | 9.91                |
| 40.0    | "                                | "  | 2.68                       | 4.68  | 35.2                |
| 20.3    | CH <sub>3</sub>                  | "  | 1.76                       | 1.97  | 2.55                |
| 30.4    | "                                | "  | 2.77                       | 6.56  | 8.38                |
| 38.6    | "                                | "  | 1.38                       | 3.28  | 28.3                |
| 15.0    | "                                | "  | 1.42                       | 4.68  | 1.21                |
| 20.0    | "                                | "  | 1.95                       | 3.82  | 2.29                |
| 30.0    | "                                | "  | 1.95                       | 3.82  | 8.46                |
| 40.0    | "                                | "  | 1.42                       | 4.62  | 31.1                |
| 15.0    | OCH <sub>3</sub>                 | "  | 1.91                       | 3.24  | 1.42                |
| 20.0    | "                                | "  | 2.41                       | 8.28  | 2.78                |
| 30.0    | "                                | "  | 2.41                       | 8.28  | 10.5                |
| 40.0    | "                                | "  | 2.41                       | 8.28  | 36.1                |
| 40.0    | "                                | "  | 3.66                       | 8.28  | 37.0                |
| 20.0    | N(CH <sub>3</sub> ) <sub>2</sub> | "  | 1.86                       | 3.68  | 2.00                |
| 30.0    | "                                | "  | 1.86                       | 3.68  | 7.45                |
| 30.0    | "                                | "  | 1.86                       | 14.7  | 7.41                |
| 40.0    | "                                | "  | 1.86                       | 3.68  | 24.8                |
| 40.0    | "                                | "  | 3.72                       | 3.68  | 25.9                |

(Continued)

TABLE XI (Continued)

| T<br>°C | R               | x  | [triene] x10 <sup>5</sup><br>M | [(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N] x10 <sup>4</sup><br>M | k x10 <sup>4</sup><br>sec <sup>-1</sup> |
|---------|-----------------|----|--------------------------------|---|---|
| 20.0    | Cl              | Cl | 2.17                           | 4.61  | 0.47                                    |
| 30.0    | "               | "  | 3.56                           | 10.7  | 1.76                                    |
| 40.0    | "               | "  | 5.85                           | 14.2  | 6.28                                    |
| 40.0    | "               | "  | 1.95                           | 4.73  | 6.17                                    |
| 20.0    | F               | "  | 4.11                           | 4.44  | 0.43                                    |
| 25.3    | "               | "  | 2.16                           | 4.54  | 0.84                                    |
| 30.0    | "               | "  | 2.16                           | 4.54  | 1.54                                    |
| 30.0    | "               | "  | 4.32                           | 9.08  | 1.58                                    |
| 30.0    | "               | "  | 2.16                           | 18.2  | 1.55                                    |
| 40.0    | "               | "  | 4.32                           | 9.08  | 5.23                                    |
| 20.0    | NO <sub>2</sub> | Br | 3.13                           | 20.0  | 1.04                                    |
| 30.0    | "               | "  | 1.75                           | 39.8  | 3.62                                    |
| 30.0    | "               | "  | 3.35                           | 19.9  | 3.66                                    |
| 30.0    | "               | "  | 2.17                           | 10.0  | 3.62                                    |
| 30.0    | "               | "  | 2.11                           | 2.00  | 3.65                                    |
| 30.0    | "               | "  | 1.74                           | 0.20  | 3.63                                    |
| 40.0    | "               | "  | 3.65                           | 20.0  | 11.9                                    |
| 40.0    | "               | "  | 2.08                           | 2.00  | 12.1                                    |

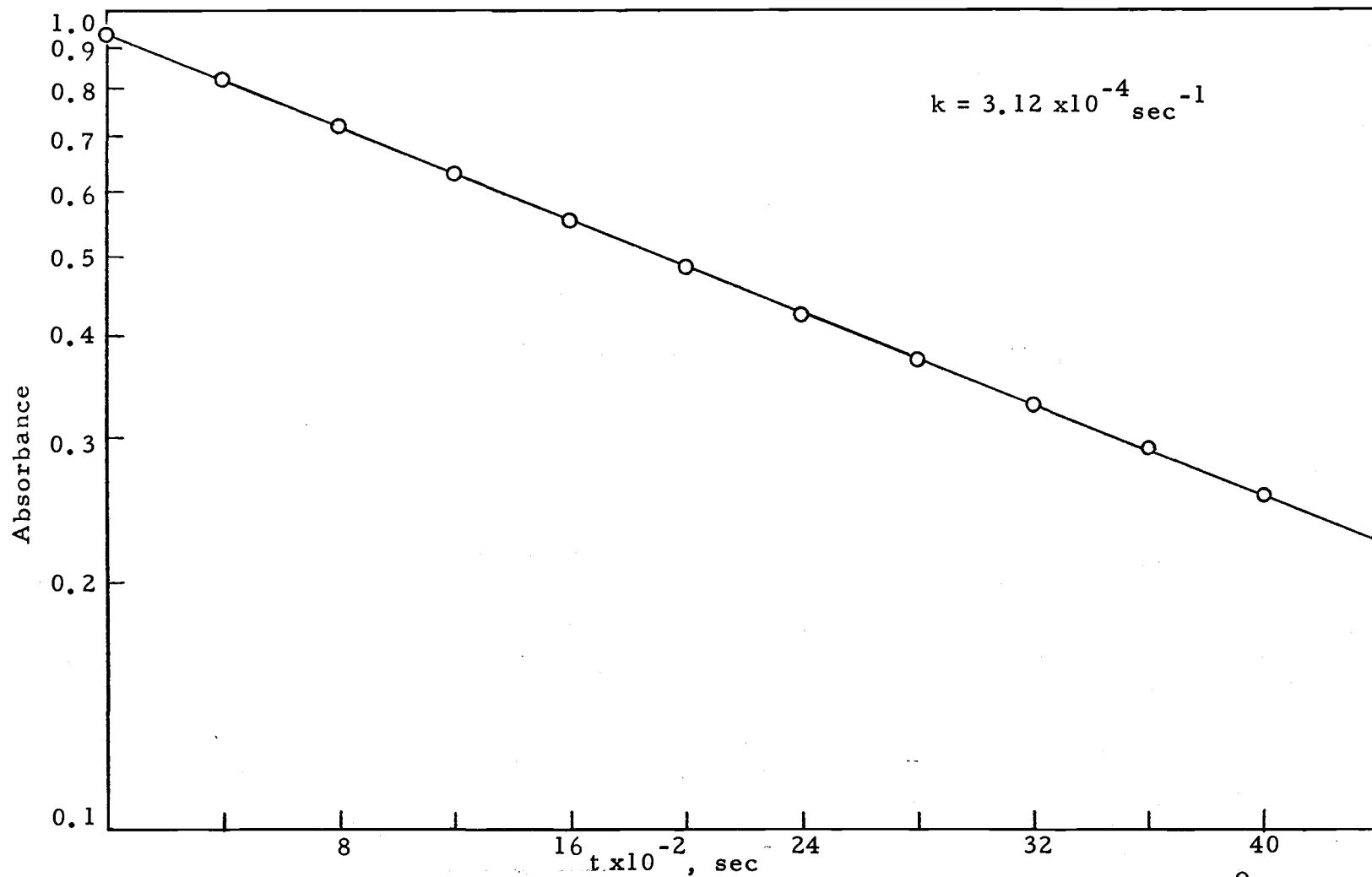


Figure 8. Plot of logarithm of absorbance of VII vs. time in buffered methanol, at  $39.2^{\circ}\text{C}$ .  
 $[\text{VII}] = 2.13 \times 10^{-5}$ ,  $[\text{Et}_3\text{N}] = 2.20 \times 10^{-4}$ ,  $[\text{HOBz}] = 4.04 \times 10^{-4}$ ,  $[\text{NaOBz}] = 4.00 \times 10^{-3}$ .

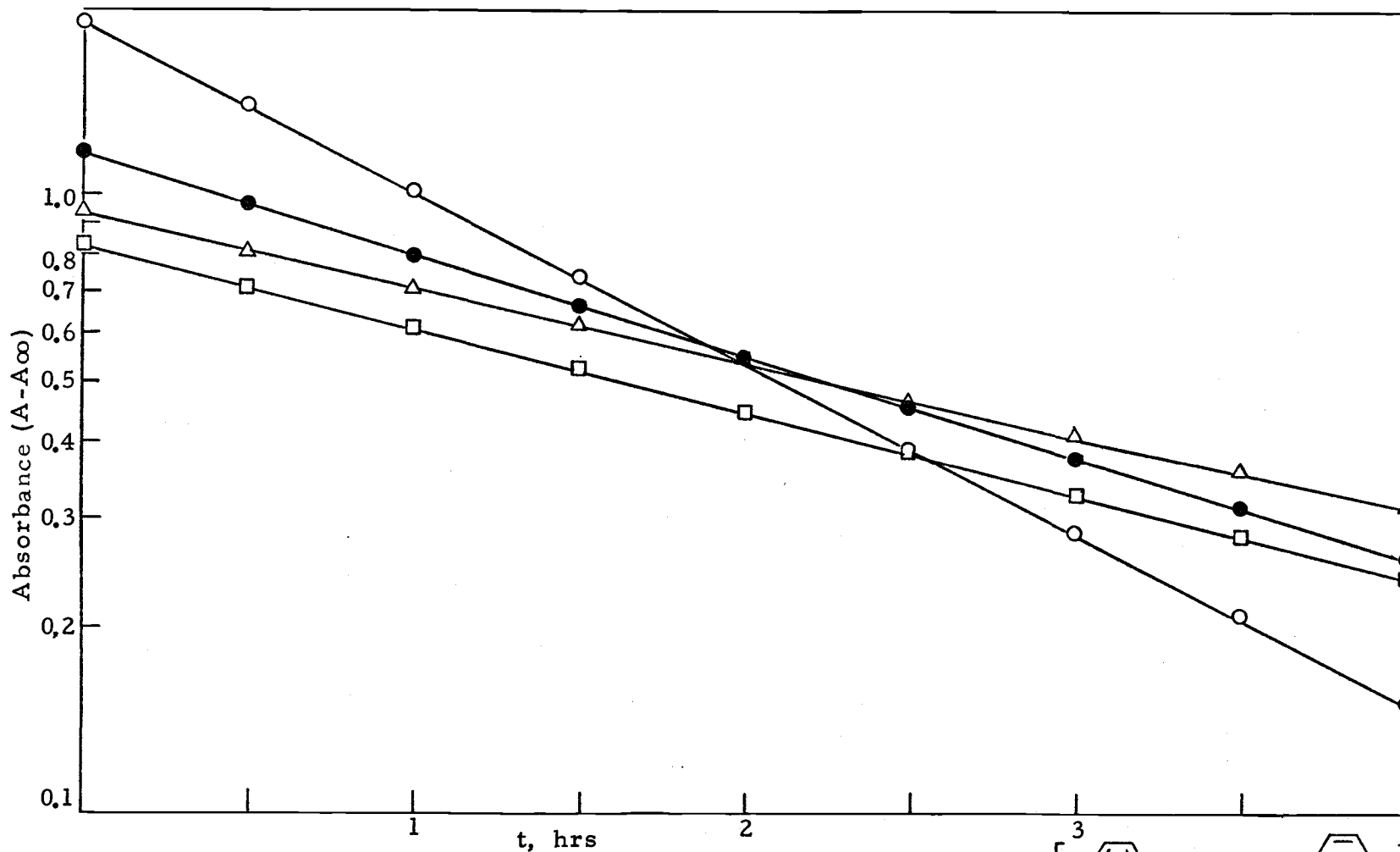


Figure 9. Plots of logarithm of  $(A - A_{\infty})$  vs. time for the ring closures of  $[\text{R}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_5=\text{N}-\text{C}_6\text{H}_4-\text{R}]^+\text{Cl}^-$  in methanol in presence of excess triethylamine,  $T=30^\circ\text{C}$ . O, R=Cl; ●, R=OMe; Δ, R=NMe<sub>2</sub>; □, R=Me.

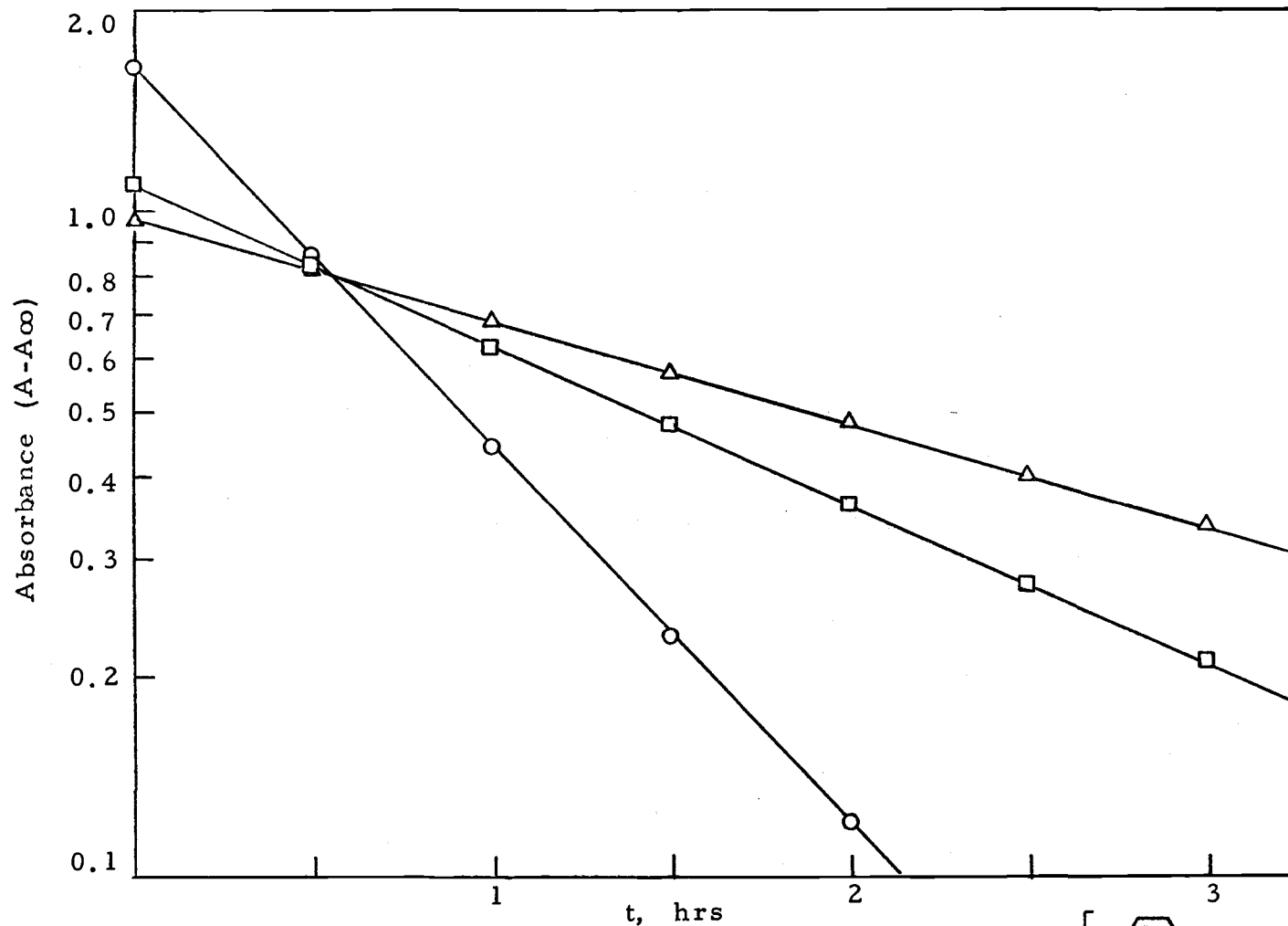


Figure 10. Plots of logarithm of  $(A - A_{\infty})$  vs. time for the ring closures of  $\left[ \text{R} - \text{C}_6\text{H}_4 - \text{N}(\text{CH}_2)_5 = \text{N} - \text{C}_6\text{H}_4 - \text{R} \right]_x^{\pm}$  in methanol in presence of excess added triethylamine at  $30^\circ\text{C}$ . ○, R=NO<sub>2</sub>, x=Br; □, R=F, x=Cl; △, R=H, x=Cl.



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