

REACTIONS OF PHOSPHORUS AZIDES WITH NORBORNYLENE AND  
N,N-DIMETHYL-2-METHYLPROPENYLAMINE. A KINETIC  
STUDY OF THE REACTION OF DIETHYL PHOS-  
PHORAZIDATE WITH NORBORNYLENE

By

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TABLE OF CONTENTS

	Page
INTRODUCTION . . . . .	x
Chapter	
I. HISTORICAL . . . . .	1
The Reactions of Azides with Alkenes. . . . .	1
Reaction Kinetics by Differential Thermal Analysis. . . . .	17
II. RESULTS AND DISCUSSION . . . . .	20
III. EXPERIMENTAL . . . . .	55
Preparation of Diethyl Phosphorazidate. . . . .	55
Preparation of Diethyl (3a,4,5,6,7,7a-Hexahydro-4,7,- methano-1H-benzotriazol-1-yl)phosphonate. . . . .	56
Preparation of 2-Norbornylidene-P,P-diphenylphosphinic Amide . . . . .	56
Preparation of Diethyl-2-norbornylidene-phosphor- amidate . . . . .	57
Hydrolysis of Diethyl-2-norbornylidene-phosphoramidate. . . . .	58
Hydrolysis of 2-Norbornylidene-P,P-diphenylphosphinic Amide . . . . .	59
Preparation of N-(P,P-Diphenylphosphinyl)-N',N'-di- methylisobutyramidine . . . . .	59
Preparation of N-(Diethylphosphoryl)-N',N'-dimethyl- isobutyramidine . . . . .	60
Preparation of N-(Di-n-butylphosphoryl)-N',N'-dimethyl- isobutyramidine . . . . .	61
Hydrolysis of N-(P,P-Diphenylphosphinyl)-N',N'-dimethyl- isobutyramidine . . . . .	62
Analysis of N-(P,P-Diphenylphosphinyl)-N',N'-dimethyl- isobutyramidine for Ammonia and Dimethylamine . . . . .	63
Gas Chromatographic Analysis of N-Phosphorylated Amidines. . . . .	63
Attempted Reduction of Triazoline with Raney Nickel . . . . .	63
Photolysis of Triazoline. . . . .	65
Procedure for Determination of the Kinetics of Forma- tion of Triazoline by Ultraviolet Spectroscopy. . . . .	65
Procedure for Determination of Kinetics of Formation of Triazoline by NMR. . . . .	68
Analysis of Norbornylene Solutions by NMR . . . . .	72

Chapter	Page
Differential Thermal Analysis Apparatus . . . . .	72
The Rate of Decomposition of Triazoline by Differential Thermal Analysis. . . . .	77
Kinetics of the Reaction of N,N-dimethylaniline and Ethyl Iodide by Differential Thermal Analysis . . . . .	82
The Enthalpy of Triazoline Decomposition by Differ- ential Thermal Analysis . . . . .	84
Apparatus for the Measurement of Rate of Nitrogen Evolution During the Decomposition of Triazoline. . . . .	85
Procedure for Measurement of Rate of Nitrogen Evolu- tion During the Decomposition of Triazoline . . . . .	86
Calculation of Activation Energy and Entropy of Activ- ation for the Decomposition of Triazoline . . . . .	88
Calculation of the Rate Constants for the Decomposition of Triazoline . . . . .	88
 BIBLIOGRAPHY . . . . .	 120

LIST OF TABLES

Table	Page
I. Phosphorus Azides . . . . .	3
II. Formation Kinetics of Triazoline . . . . .	30
III. Temperature Dependence of Rate Constants $k_a$ and $k_b$ . . . . .	40
IV. Solvent Dependence of Rate Constants $k_a$ and $k_b$ . . . . .	41
V. Formation of Triazoline by NMR, Run 1. . . . .	70
VI. Formation of Triazoline by NMR, Run 2. . . . .	71
VII. Formation of Triazoline by NMR, Run 3. . . . .	73
VIII. Formation of Triazoline by NMR, Run 4. . . . .	74
IX. Analysis of Norbornylene Solutions by NMR. . . . .	75
X. Decomposition of Triazoline by DTA, Run 2. . . . .	78
XI. Decomposition of Triazoline by DTA, Run 3. . . . .	79
XII. Decomposition of Triazoline by DTA, Run 35 . . . . .	80
XIII. Calibration of DTA Apparatus . . . . .	83
XIV. Decomposition of Triazoline in Diglyme at 371 <sup>o</sup> K. . . . .	89
XV. Decomposition of Triazoline in Diglyme at 381 <sup>o</sup> K. . . . .	90
XVI. Decomposition of Triazoline in Diglyme at 391 <sup>o</sup> K. . . . .	91
XVII. Decomposition of Triazoline in Diglyme at 399 <sup>o</sup> K. . . . .	92
XVIII. Decomposition of Triazoline in Diglyme at 381 <sup>o</sup> K. . . . .	93
XIX. Decomposition of Triazoline in Toluene at 381 <sup>o</sup> K. . . . .	94
XX. Decomposition of Triazoline in Benzonitrile at 381 <sup>o</sup> K . . . . .	95

LIST OF ILLUSTRATIONS

Plate		Page
Nuclear Magnetic Resonance Spectra		
I.	Diethyl (3a,4,5,6,7,7a-Hexahydro-4,7-methano-1H-benzotriazol-1-yl)phosphonate . . . . .	99
II.	Diethyl Phosphorazidate. . . . .	100
III.	Diethyl 2-Norbornylidinephosphoramidate. . . . .	101
IV.	N-(Di-n-butylphosphoryl)-N',N'-dimethylisobutyramidine . .	102
V.	N-(P,P-Diphenylphosphinyl)-N',N'-dimethylisobutyramidine .	103
VI.	N-(Diethylphosphoryl)-N',N'-dimethylisobutyramidine. . . .	104
Infrared Spectra		
VII.	Diethyl (3a,4,5,6,7,7a-Hexahydro-4,7-methano-1H-benzotriazol-1-yl)phosphonate . . . . .	105
VIII.	Diethyl Phosphorazidate. . . . .	106
IX.	Diethyl 2-Norbornylidinephosphoramidate. . . . .	107
X.	2-Norbornylidine-P,P-diphenylphosphinic Amide. . . . .	108
XI.	N-(Di-n-butylphosphoryl)-N',N'-dimethylisobutyramidine . .	109
XII.	N-(P,P-Diphenylphosphinyl)-N',N'-dimethylisobutyramidine .	110
XIII.	N-(Diethylphosphoryl)-N',N'-dimethylisobutyramidine. . . .	111
XIV.	Diphenylphosphinyl Azide . . . . .	112
XV.	Reaction Mixture of Triazoline, Diethyl Phosphorazidate and Norbornylene . . . . .	113
XVI.	Reaction Mixture of Diphenylphosphinyl Azide and N,N-dimethyl-2-methylpropenylamine . . . . .	114

Plate		Page
-------	--	------

Ultraviolet Spectra

XVII.	Diethyl Phosphorazidate. . . . .	115
XVIII.	Diethyl (3a,4,5,6,7,7a-Hexahydro-4,7-methano-1H-benzotriazol-1-yl)phosphonate . . . . .	116
XIX.	Diethyl 2-Norbornylidene phosphoramidate. . . . .	117

Photographs

XX.	Apparatus for Measurement of Nitrogen Evolution by Conventional Method . . . . .	118
XXI.	Differential Thermal Analysis Apparatus. . . . .	119



## LIST OF FIGURES

Figure	Page
1. Arrhenius Plot for the Formation of Triazoline. . . . .	31
2. Apparatus for Measurement of Nitrogen Evolution by Conventional Method . . . . .	33
3. Arrhenius Plot of $k_a$ for the Decomposition of Triazoline. . .	38
4. Arrhenius Plot of $k_b$ for the Decomposition of Dipolar-ion IV. . .	39
5. Differential Thermal Analysis Apparatus . . . . .	45
6. Differential Thermal Analysis Curve for the Decomposition of Triazoline. . . . .	49
7. Comparison of Differential Thermal Analysis Data and Data Obtained by Conventional Methods for the Reaction of N,N-Dimethylamine with Ethyl Iodide . . . . .	50
8. Arrhenius Plot of Differential Thermal Analysis Data for the Decomposition of Triazoline . . . . .	52
9. Arrhenius Plot for the Decomposition of Triazoline; Comparison of Conventional Method and Differential Thermal Analysis. . . . .	53
10. Plot of Raw Data for the Formation of Triazoline. . . . .	67
11. Calibration of Nitrogen Evolution Apparatus . . . . .	87

## INTRODUCTION

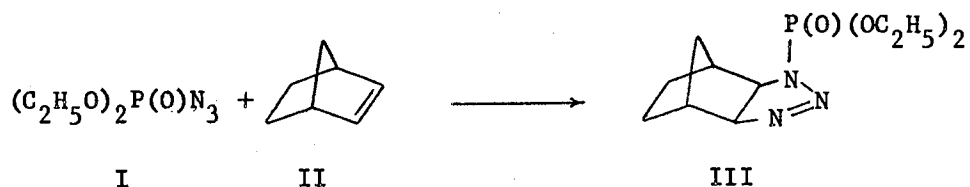
Reactions of aryl azides with electron-rich alkenes has been reported to give triazoline intermediates which decompose to give the corresponding aziridines and imines. Similar reactions of phosphoryl azides have not been reported until now. Treatment of diethyl phosphorazidate and diphenylphosphinyl azide with highly reactive unsaturated molecules has resulted in the synthesis of several new compounds containing P-N bonds. Phosphoryl amidines and amidates are rare classes of organophosphorus materials that were realized from this study. A kinetic analysis of the reaction of diethyl phosphorazidate and norbornylene demonstrated the formation of a triazoline intermediate.

# CHAPTER I

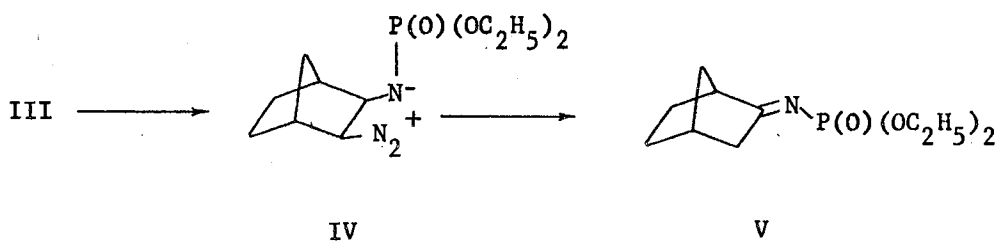
## HISTORICAL

### The Reaction of Azides with Alkenes

Recently it has been reported from this Laboratory<sup>12, 14</sup> that diethyl phosphorazidate (I) reacts with norbornylene (II) to give a relatively stable triazoline III.

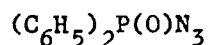


Triazoline III decomposed via a dipolar ion IV to give diethyl-2-norbornylidene phosphoramidate (V) at temperatures greater than  $70^\circ$ .



This is the only example reported where a triazoline is formed in the

reaction of a phosphorus azide with an alkene. Franz and Osuch<sup>28</sup> have reported that diphenylphosphinyl azide (VI) reacted with

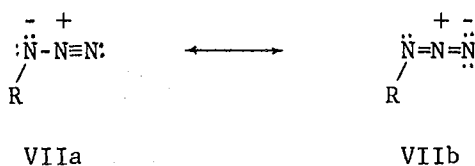


## VI

bicyclic alkenes such as II to form aziridines and imines. No evidence for the formation of a triazolone intermediate was cited.

The chemistry and properties of organic azides<sup>19</sup> and inorganic azides<sup>5, 27, 36</sup> have been reviewed extensively. Covalently-bonded azides in general are prepared, usually in high yield, by reacting on alkali metal azide such as  $\text{NaN}_3$  or  $\text{LiN}_3$  with a halide. The first organic azide (phenyl azide) was prepared by P. Griess<sup>35, 34</sup> in 1864. Since 1890 when Curtius began his work on the now well-known degradation of acyl azides,<sup>77</sup> organic azides have been the topic of many investigations. Table I summarizes the phosphorus azides that have been prepared to date.

Electronic structural studies<sup>23</sup> and electron diffraction studies<sup>66</sup> on alkyl azides indicate that alkyl substituents are at an angle of about  $120^\circ$  with the linear  $\text{N}_3$  moiety where  $\text{R} = \text{CH}_3$ . Where  $\text{R} = \text{H}$  the  $\text{R}-\text{N}_3$  angle is  $113^\circ$ .



Although octet stabilized contributing structures VIIa,b partially explain the observed electronic spectra and electron diffraction patterns, sextet structures VIIc-e can be written,<sup>44</sup>

TABLE I

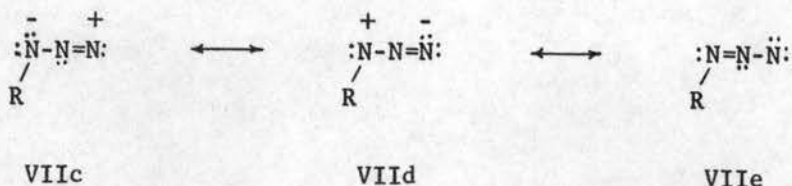
## PHOSPHORUS AZIDES

Compound <sup>a</sup>	M. p.	B.p./mm.	Refractive Index	Yield, %
$(C_6H_5)_2PN_3$ <sup>65</sup>	13.6-13.8° (d)	---	---	68
$(CF_3)_2PN_3$ <sup>59</sup>	glass at -196°			
$(CH_3O)_2P(O)N_3$ <sup>47</sup>	---	79.5-81°/10	$n_D^{20}$ , 1.4276	34.8
$(C_2H_5O)_2P(O)N_3$ <sup>47,74</sup>	---	76-77°/4.5	$n_D^{20}$ , 1.4260	62.8
$(n-C_4H_9O)_2P(O)N_3$ <sup>11</sup>	---	103-104°/0.8	$n_D^{25}$ , 1.4333	87
$(C_6H_5)_2P(O)N_3$ <sup>7,8</sup>	---	137-140°/0.05	$n_D^{20}$ , 1.6077	87
$(p-CH_3C_6H_4)_2P(O)N_3$ <sup>7</sup>	---	190-195/0.5	---	---
$(p-ClC_6H_4)_2P(O)N_3$ <sup>7</sup>	---	160-165/0.005	$n_D^{20}$ , 1.6246	---
$(CH_3)_2P(S)N_3$ <sup>73</sup>	68°	---	---	80
$(C_2H_5)_2P(S)N_3$ <sup>73</sup>	---	oil	---	91
$(CH_3)(CH_3S)P(S)N_3$ <sup>72</sup>	---	---	---	---
$(C_2H_5O)(CH=CH)P(S)N_3$ <sup>68,71,72</sup>	---	---	---	---
$(C_6H_5)_2P(S)N_3$ <sup>7</sup>	---	---	---	---

TABLE I (continued)

$[(\text{CH}_3)_2\text{N}]_2\text{P}(\text{O})\text{N}_3$ <sup>82</sup>	---	93-94°/2.0	$n_{\text{D}}^{21}$ , 1.4673	75
$[(\text{CH}_3)_2\text{N}]_2\text{P}(\text{S})\text{N}_3$ <sup>82</sup>	---	80°/1.5	$n_{\text{D}}^{21}$ , 1.5177	---
$(\text{C}_6\text{H}_5)_2\text{P}(\text{NTos})\text{N}_3$ <sup>17</sup>	220(d)	---	---	---
$\text{C}_6\text{H}_5\text{P}(\text{O})(\text{N}_3)_2$ <sup>6</sup>		72-74°/0.1	$n_{\text{D}}^{20}$ , 1.5690	---
$\text{C}_6\text{H}_5\text{P}(\text{S})(\text{N}_3)_2$ <sup>6</sup>		explodes	---	---
$\text{C}_6\text{H}_5\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]\text{N}_3$ <sup>6</sup>		86-88°/10 <sup>-3</sup>	$n_{\text{D}}^{20}$ , 1.5473	---
$\text{C}_6\text{H}_5\text{P}(\text{O})(\text{Cl})\text{N}_3$ <sup>6</sup>	---	65-67°/0.75	$n_{\text{D}}^{20}$ , 1.5636	---
$\text{C}_6\text{H}_5\text{P}(\text{O})[\text{NP}(\text{C}_6\text{H}_5)_3]\text{N}_3$ <sup>6</sup>	143-145	---	---	---
$(\text{B}_{10}\text{H}_{10}\text{C}_2\text{PN}_3)_2$ <sup>4</sup>	180°(d)	---	---	quant.
$\text{P}_3\text{N}_3(\text{NH}_2)_2(\text{N}_3)_4$ <sup>22</sup>	81-82°	---	---	20
$\text{P}_3\text{N}_3(\text{N}_3)_6$ <sup>38</sup>	---	unstable oil	---	---

<sup>a</sup>Azides listed above were prepared by reacting  $\text{MN}_3$  (M = Na or Li) with the corresponding phosphorus chloride.



These structures probably contribute little if at all to the ground state because there was no observed solvent effect<sup>23</sup> for the electronic transitions. A solvent effect would be expected with a change in dipole moment that would occur in these transitions if VIIc-e made important contributions to the ground state.

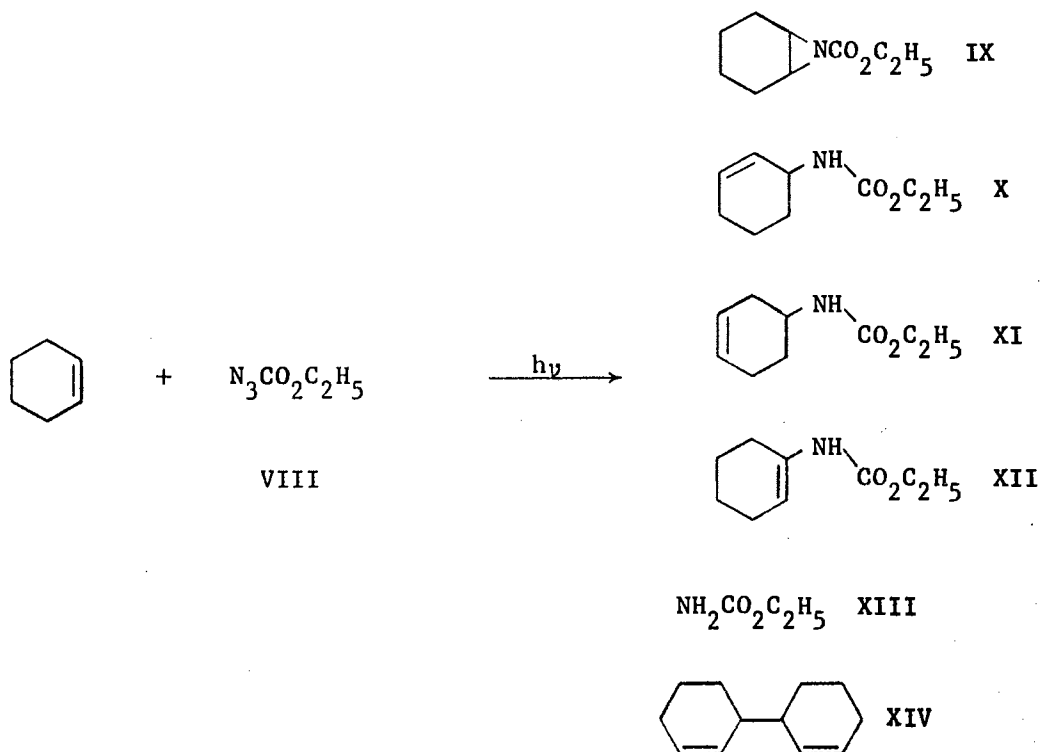
The azide group is electron withdrawing with respect to carbon.<sup>23</sup> The Hammett sigma constant has been estimated to be about the same as chlorine which is +0.23 ( $\sigma_p$ ).<sup>37</sup>

Reactions of azides fall into three general classes. Azides decompose thermally, photolytically or by electric discharge with loss of nitrogen to form reactive intermediates<sup>1, 39</sup> (nitrenes) R-N: which are isoelectronic with carbenes. In the second class are included the condensations with phosphines to form phosphoranes,<sup>48</sup> and the reactions where N<sub>3</sub> is lost by nucleophilic displacement. Phosphorus azides are unique<sup>7, 6</sup> in many of the chemical transformations in this class. In the third class azides react as enophiles in 1,3-dipolar additions.<sup>44</sup>

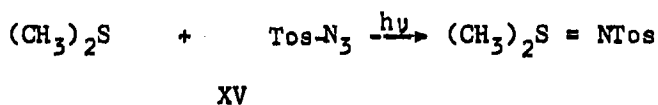
Formation of nitrenes by thermal or photolytic decomposition of azides is well documented.<sup>1, 39</sup> Hydrazoic acid<sup>48</sup> decomposes to :NH at 4.2°K. in an argon matrix under photolytic conditions. The presence of :NH was demonstrated by ultraviolet spectroscopy. Phenyl azide decomposes thermally or photolytically<sup>39</sup> to give azobenzene, aniline and resinous

products. Evidence for a nitrene intermediate was supported by the fact that when mixtures of substituted phenyl azides were photolyzed, mixed azo compounds were formed.

Acyl, sulfonyl and phosphazo azides also give nitrene intermediates under photolytic conditions. Ethyl azidoformate (VIII) reacts with cyclohexene to give an aziridine IX insertion products X-XII, ethyl urethane (XIII) and 2,2'-dicyclohexene<sup>30, 31</sup> (XIV).



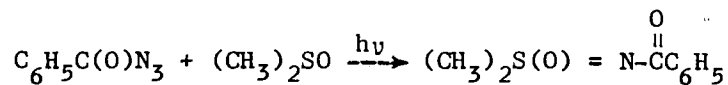
The nitrene formed when tosyl azide (XV) is decomposed under photolytic conditions has been trapped with dimethyl sulfide.<sup>40</sup>



Similarly benzoyl azide XVI reacts with dimethyl sulfoxide to give an



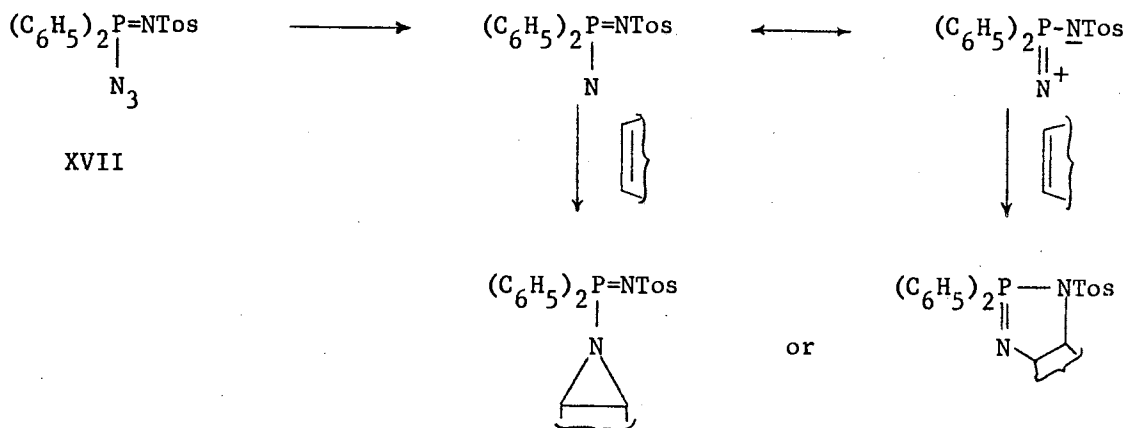
N-benzoyl sulfoximine.



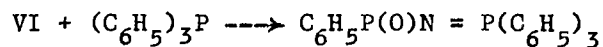
XVI

Dermer and Edmison<sup>25</sup> have demonstrated that benzenesulfonyl azide decomposes thermally to an intermediate which is capable of initiating vinyl polymerizations. A nitrene is suspect.

The only phosphorus azide reported to give a nitrene intermediate is P, P-diphenyl-N-tosylphosphazene azide (XXII).<sup>17</sup> The proposed nitrene was trapped by reaction with the strained double bond of dicyclopentadiene.



The reaction of azides with phosphine to form phosphoranes was first studied by Staudinger in 1919.<sup>79</sup> Diphenylphosphinyl azide (VI) reacts with triphenylphosphine to give the corresponding phosphorane.<sup>8</sup>

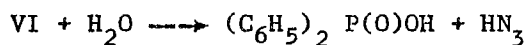


Similarly benzenesulfonyl azide (XVIII) and triphenylphosphine give the corresponding phosphorane.<sup>51</sup>



## XVIII

Phosphorus azides behave in an unusual manner in reactions with nucleophiles such as ammonia, amines, water and alcohols.<sup>8</sup> For instance diphenylphosphinyl azide (VI) and water form diphenylphosphinic acid (XIX).

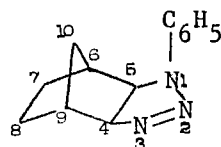


## XIX

Benzenesulfonyl azide (XVIII) and acyl azides can be prepared in water while reaction of alcohols and amines with phosphorus azides give the corresponding displacement products.

Azides as enophiles in 1,3-dipolar addition reactions constitute but a small portion of this class of condensations which has been reviewed by Huisgen.<sup>44</sup> Since this is such a large group which includes nearly all azides, the discussion will be limited primarily to reactions of azides which are substituted with electron-withdrawing groups.

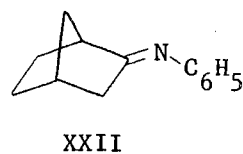
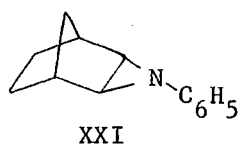
In 1893 Michael<sup>59</sup> obtained 1-phenyl-1,2,3-triazol-4,5-dicarboxylic ester from the reaction of phenyl azide and acetylene dicarboxylic ester. Since then the reaction of azides with acetylenes to form 1,2,3-triazoles and with alkenes to form  $\Delta^2$ -triazolines, has become a general method for the preparation of such compounds. In 1933, Alder<sup>2</sup> examined the reaction of phenyl azide with norbornylene (II) which gave the triazoline XX and thus demonstrated the relative strain of this double bond



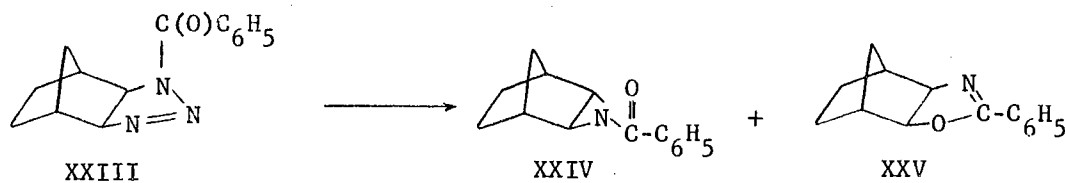
## XX

as compared with the double bond of bicyclo[2.2.2.]octene which did not react with phenylazide. That the adduct XXXII was exo rather than endo was shown by the fact that condensation did not occur<sup>3</sup> if the 1 carbon bridge was substituted.

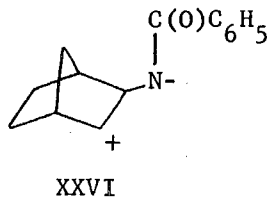
Stability of the triazoline formed by the 1,3-dipolar addition of azides to alkenes is sensitive to the nature of the 4-substituent. Triazoline XX is stable at temperatures below 150°. Decomposition occurs at temperatures greater than 150° with loss of nitrogen to give aziridine XXI and imine XXII.<sup>2</sup>



Triazoline XXIII formed from benzoyl azide (XVI) and norbornylene (II) decomposes at 40° to give an aziridine XXIV and an oxazoline XXV.<sup>44</sup>



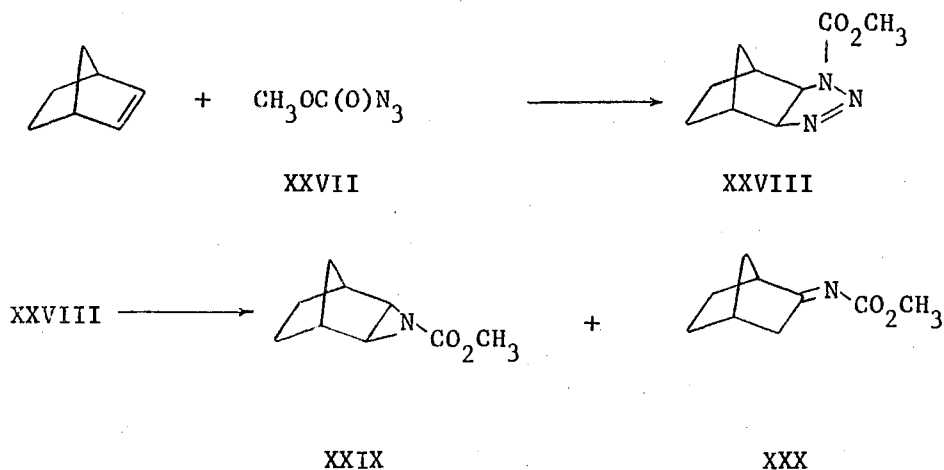
The decomposition has been proposed to proceed via a dipolar ion XXVI.<sup>44</sup>



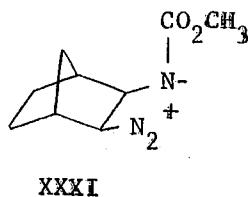
No evidence has been published to substantiate this mechanism which is difficult to accept in total since rearrangements of norbornyl cations such as XXVI are well known.<sup>15</sup>

Methyl azidoformate (XXVII) reacted with norbornylene (II) at room

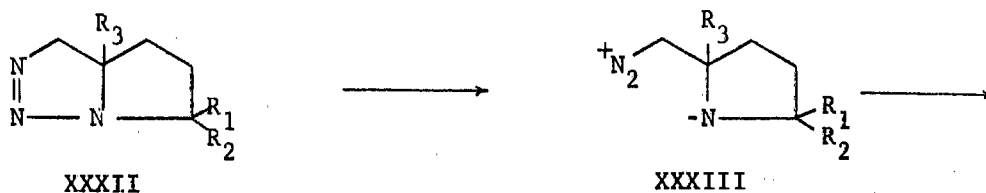
temperature and gave an unstable triazoline XXVIII which decomposed in boiling toluene. A mixture of aziridine XXIX and imine XXX resulted.<sup>63</sup>

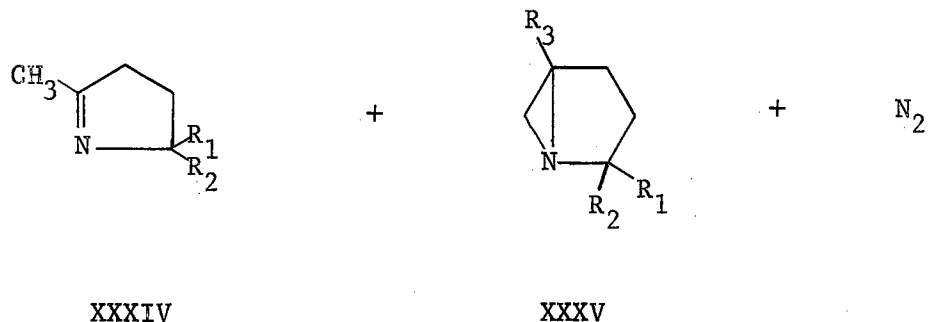


Formation of XXIX and XXX was thought to proceed via a dipolar ion intermediate XXXI.



Unfortunately the only evidence for this intermediate<sup>63</sup> was based on the observation that the rate of decomposition of XXVIII as evidenced by nitrogen evolution increased 3 fold when triglyme and 20 fold when dimethyl sulfoxide as solvents were substituted for 1,1-diphenylmethane. Logothetis<sup>53</sup> presented similar evidence for the formation of a dipolar ion XXXIII during the decomposition of triazoline XXXII which lead to XXXIV and XXXV.





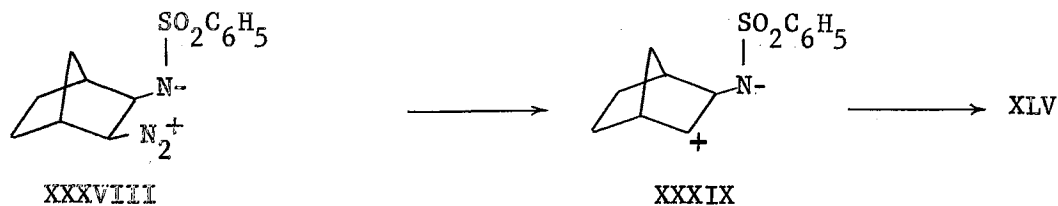
Decomposition of XXII proceeded at a 10 fold rate in nitromethane and a 20 fold rate in aqueous diglyme as compared to the reaction in toluene.

Azides substituted with powerful electron-withdrawing groups such as benzenesulfonyl azide (XVIII) and cyanogen azide (XLI) react rapidly with electron-rich alkenes such as norbornylene (II). Apparently the substituent weakens the triazoline mesomerism so that it decomposes almost as rapidly as it forms. Franz<sup>29</sup> has suggested a mechanism similar to epoxidation as operative in the reaction of benzenesulfonyl azide (XVIII) with norbornylene (II).

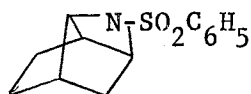


This speculation was offered on the basis that only XXXVII was obtained in the reaction of benzenesulfonyl azide (XVIII) with norbornylene (II). Oehlschlager and Zalkow<sup>64</sup> observed similar results with the same reaction. They proposed that the reaction does indeed proceed via a triazoline intermediate which decomposed rapidly to a diazonium ion XXXVIII similar to XXXI. Decomposition of the ion to the dipolar ion XXXIX and subsequent

formation of XXXVII must be very rapid or concerted since skeletal rearrangements of XXXIX would be expected.<sup>15</sup>



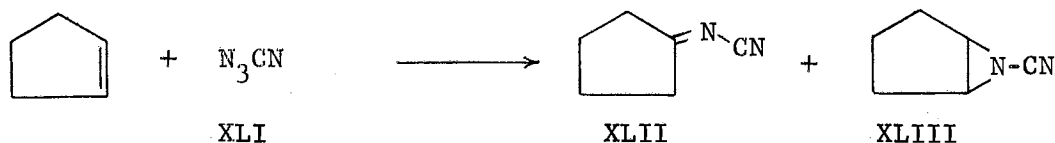
Rearrangements of carbonium ions<sup>15</sup> such as XXXIX are known to occur rapidly to give 2,7-products such as XL.



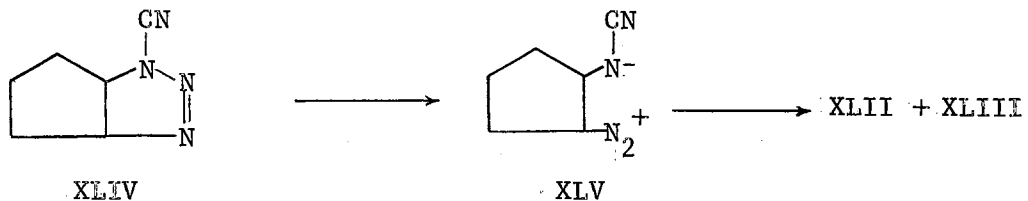
XL

Azetidine XL has not been isolated in this reaction.<sup>29, 64</sup> Conclusions involving XXXVIII are thus drawn deductively on the basis of decomposition of triazolines already discussed.

Cyanogen azide (XL) reacted<sup>58, 57</sup> with cyclopentene to give an imine XLII and an aziridine XLIII.



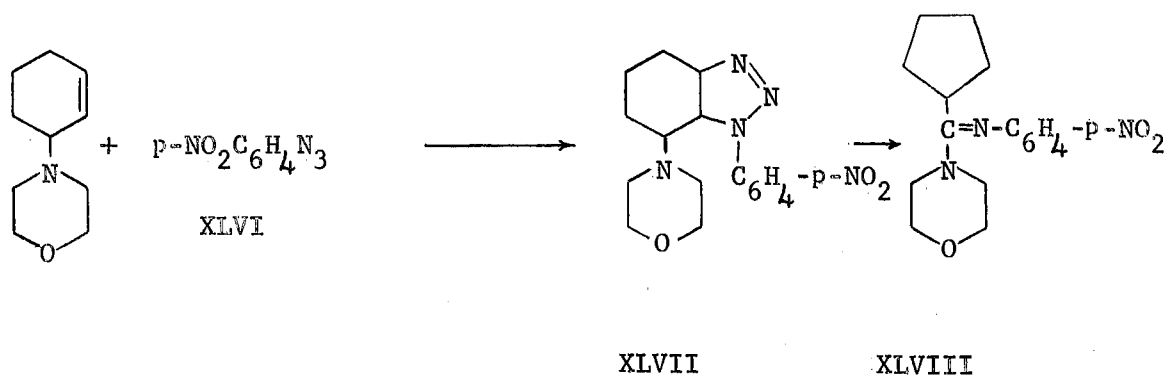
A mechanism proposed included a triazoline intermediate XLIV which decomposed without detection to products via a dipolar ion XLV of similar structure to those ions already described, namely, IV, XXXII and XXXVIII.



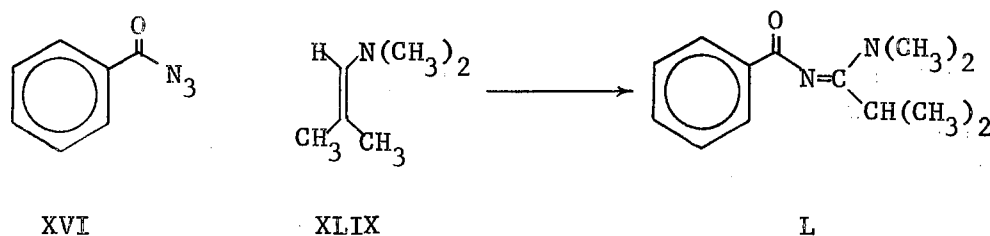
Unpublished kinetic evidence was cited in support of a dipolar ion XLV intermediate in this reaction.<sup>58</sup>

Azides substituted with electron-withdrawing groups react with enamines<sup>80</sup> to form amidines.<sup>21, 13</sup> Aryl azides<sup>33, 31, 61</sup> condense with enamines to give an intermediate triazoline which can be isolated and which decompose with loss of nitrogen to amidines. A dipolar ion intermediate has also been proposed in this decomposition.

p-Nitrophenyl azide<sup>31</sup> and XLVI give triazoline XLVII, which upon heating to 150°, decomposes with loss of nitrogen and yields amidine XLVIII.

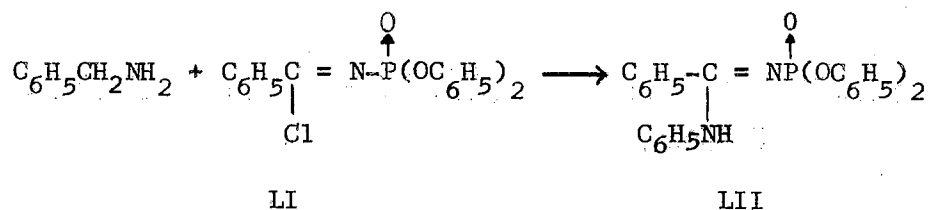


Burpitt<sup>21</sup> reported recently that benzoyl azide (XVI) reacted with N,N-dimethyl-2-methylpropylamine (XLIX) to form N-benzoyl-N',N'-dimethylisobutyramidine (L).



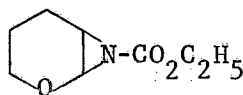
The mechanism of formation of the observed product L has not been studied. The products in such reactions are thought to result<sup>33</sup> from decomposition of a triazoline (formed by a 1,3-dipolar addition of azide to enamine) which may decompose to a dipolar ion intermediate.

Several phosphorylated amidines have been prepared by treatment of an amine with the corresponding halide. This class of compound has been reviewed by Sasse.<sup>68</sup> An example is the preparation of N-diphenoxyphosphoryl-benzamide (LII) <sup>24</sup> from N-(diphenyl-phosphoryl)-(benzimidide-chloride) (LI) and benzylamine.



To date the only direct syntheses of phosphorylated amidines from enamines and phosphorus azides has been reported from this Laboratory.<sup>13</sup>

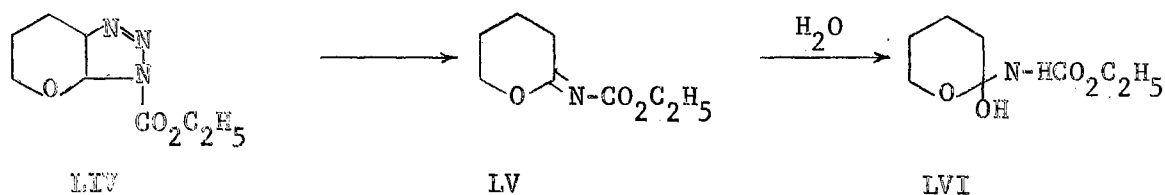
Reaction of azides and vinyl ethers has also been studied.<sup>11, 20, 46</sup> Brown and Edwards<sup>20</sup> observed that photolysis of a mixture of ethyl azidoformate VIII and dihydropyran gave an aziridine LIII.



LIII

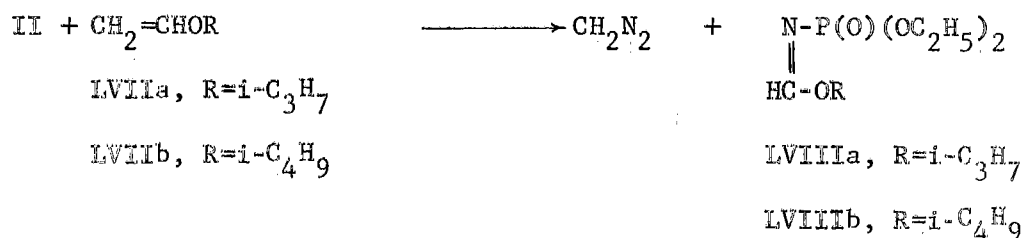
Thermal decomposition (boiling dihydropyran) of proposed intermediate triazoline LIV gave LV which probably formed from imidate LVI upon addition of aqueous dioxane.





The steric course of additions of azides to vinyl ethers was studied by Huisgen and Szeimes<sup>46</sup> who stated the reaction was 97% stereoselective favoring cis products. This indicated that the 1,3-dipolar addition is concerted or at least the reaction to form a triazoline proceeded rapidly before inversion (resulting from free rotation around the C-C bond) could occur.

Recently data by Berlin and Khayat<sup>11</sup> from this Laboratory have substantiated that diethyl phosphorazidate (I) and vinyl ethers LVIIa,b react (with loss of nitrogen) to form N-phosphorylated imidates LVIIIa,b and diazomethane.

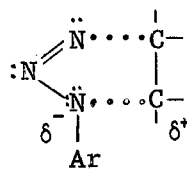


Di-n-butyl phosphorazidate (LIX) gave similar results. A triazoline intermediate was not detected but is a probable transitory intermediate in view of the loss of diazomethane.

Kinetics of formation of the products of 1,3-dipolar cycloadditions has been critically evaluated by Huisgen.<sup>45</sup> Since this review by Huisgen is concerned primarily with enophiles other than azides, it will not be discussed here.

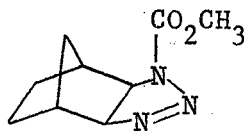
Walker and Waters<sup>84</sup> claim that organic azides decompose thermally in various media by two pathways. In inert solvents azides decompose with loss of nitrogen to give nitrenes. Product analysis and large activation energies support a nitrene intermediate. Another pathway with a lower activation energy and large entropy requirements was considered as support for the concerted process for the formation and decomposition of a triazoline intermediate. For instance, p-methoxyphenyl azide decomposed in ethyl benzoate at 133° with an activation energy of 38.5 kcal./mole, and an entropy of activation of 19.6 e.u. In indene where a triazoline could form, the activation energy was considerably less, 19.6 kcal./mole while the entropy of activation was -4.9 e.u.

In view of low dependency of rate on solvent polarity Scheiner<sup>70</sup> concluded that addition of aryl azides to norbornylene (II) to form triazolines in a concerted process. That there is some charge imbalance developed in the transition state is supported by a large Hammett substituent effect ( $\rho = +0.84$ ). The entropy of activation for the addition of phenyl azide to norbornylene was found to be -31.0 e.u. at 25° C., which is in accord with a highly ordered transition state. The enthalpy of activation for this transformation was 14.7 kcal./mole. On the basis of entropy of activation and the large substituent effect a transition state LIX was proposed in which a partial negative charge on the nitrogen could be stabilized by para-substituted electron-withdrawing groups.



LIX

Oehlschlager and Zalkow<sup>64</sup> reported similar entropy requirements for the formation of triazoline XXVIII from methyl azidoformate (XXVII) and norbornylene. The entropy of activation reported for this reaction was -29 e.u..



XXVIII

### Reaction Kinetics by Differential

#### Thermal Analysis (DTA)

Differential thermal analysis (DTA) is a thermal technique in which heat effects associated with a physical or chemical change are recorded as a function of time while a sample is heated at a constant rate. This technique has proved to be of great value to the analytical chemist, the metallurgist, the physical chemist and the ceramic chemist for the analysis of various substances. Many reviews, books and chapters in books have appeared on the subject. The book "Differential Thermal Analysis: Theory and Practice" by Smothers<sup>78</sup> contains more than 1500 references. The discussion here will be limited to that area of DTA dealing with kinetics which has not been developed or applied extensively as have other areas in this vast topic.

A number of methods have been developed for analyzing DTA data to obtain activation energies and have been reviewed by Wendlandt.<sup>85, 86, 87</sup> Basically there are two methods involving DTA that may be used to determine reaction kinetics. The first approach was developed by Kissinger<sup>49</sup> which was derived from the work of Murray and White<sup>62</sup> and Vaughn.<sup>81</sup> The

method is based on the following equation:

$$\frac{d(\ln\theta/T_m^2)}{d(1/T_m)} = -\frac{E^*}{R}$$

where  $\theta$  is  $dT/dt$  (the heating rate),  $T_m$  is the temperature at which the maximum in the DTA curve occurs,  $E^*$  the activation energy for the reaction and  $R$  is the gas constant. To obtain the activation energy ( $E^*$ ), the peak maxima temperatures ( $T_m$ ) are measured at various heating rates;  $\ln\theta/T_m^2$  versus  $1/T_m$  is plotted to give a straight line with slope  $-E^*/R$ . The reaction order ( $n$ ) is determined by examining the slope of the DTA curve for the various heating rates to obtain a quantity called the slope index ( $S$ ).<sup>49</sup> The order is then calculated from:

$$n = 1.26 S^{\frac{1}{2}}$$

Recently Levskii<sup>52</sup> has used this method to determine the reaction kinetics of decomposition of various solid inorganic compounds.

The second method is that developed by Borchardt and Daniels.<sup>18</sup> The equation derived from heat balance considerations is written:

$$k = \left[ \frac{KAV}{n_0} \right]^{x-1} \frac{C_p \frac{d\Delta T}{dt} + K\Delta T}{[K(A-a) - C_p \Delta T]^x}$$

Where  $k$  is the reaction rate constant,  $K$  is the cell constant,  $A$  is the total area under the DTA curve,  $V$  is the volume of sample and reference solutions in each cell,  $n_0$  is the initial concentration of reactant,  $x$  is the reaction order,  $\Delta T$  is difference in temperature between the sample and reference at time  $t$ ,  $a$  is the area under the curve at time  $t$  and  $C_p$  is the heat capacity of the reference which is assumed to be approximately

the same as the sample because the sample is usually dilute. For first order reactions ( $x = 1$ ) this equation simply is

$$k = \frac{C_p \frac{d\Delta T}{dt} + K\Delta T}{K(A-a) - C_p\Delta T}$$

which reduces still further to

$$k = \frac{\Delta T}{A-a}$$

on the assumption that  $C_p \frac{d\Delta T}{dt}$  and  $C_p \Delta T$  are small compared to  $K \Delta T$  and  $K(A-a)$ . Kinetics determined by these equations have been shown to be in close agreement<sup>18</sup> to data obtained by conventional procedures.

The enthalpy ( $\Delta H$ ) for the reaction being studied can also be determined from the DTA curve.<sup>18</sup> The total area (A) can be related to  $\Delta H$  by calibration of the system using a reaction for which the value of  $\Delta H$  is accurately known. From the area under this curve the cell constant (K) is determined as cal./unit area. The  $\Delta H$  for a reaction under the same condition then is the KA.

$$\Delta H = K \int_0^{\infty} \Delta T dt = KA$$

Recently a linear relationship between DTA peak areas and sample weights confirming this method has been obtained by Maeda and Azumi.<sup>56</sup>

## CHAPTER II

### RESULTS AND DISCUSSION

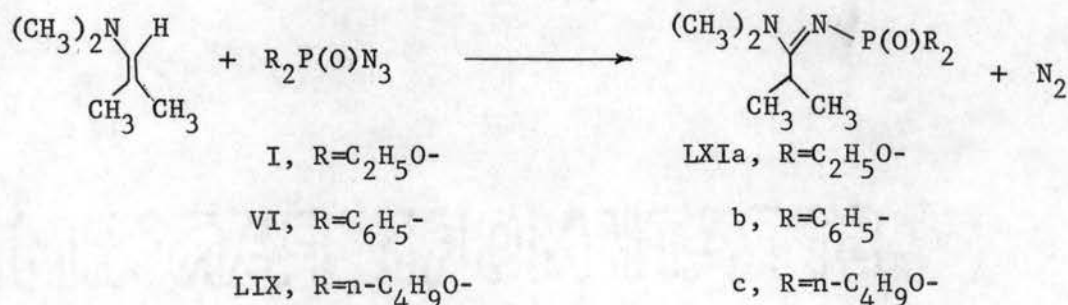
The reaction of diethyl phosphorazidate (I) with norbornylene (II) has been studied in detail. A triazoline III was formed from the condensation of I with II via a 1,3-dipolar cycloaddition as evidenced by large negative entropy requirements ( $\Delta S^* = -27.4$  e.u.) for the formation of the transition state. The triazoline appeared to be stable indefinitely in solvents at room temperature but III could not be isolated in pure form. Decomposition of triazoline III at temperatures greater than  $80^\circ$  was found to be a highly solvent-dependent reaction which followed first order kinetics with two consecutive reactions occurring in the process. Product analysis which showed that amidate V was formed in yield greater than 90%, and kinetic data ( $\Delta S^* = -8.54$  e.u. for the formation of amidate V from the dipolar ion IV) supported the conclusion that the dipolar ion IV decomposed via an ordered transition state which might be stabilized by the phosphoryl group.

Characterization of triazoline III and the product V of decomposition was accomplished by chemical and instrumental methods. 2-Norbornylidene-P,P-diphenylphosphinic amide (LXIV), the only product isolated from the reaction of diphenylphosphinyl azide (VI) and norbornylene (II), was identified by similar methods. There was no evidence for a triazoline intermediate in this transformation.

Differential thermal analysis (DTA) of the decomposition of triazoline

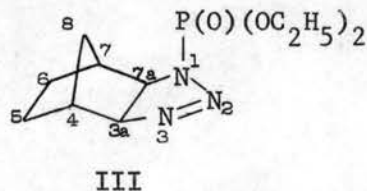
III supported the conclusion that the heat of reaction for the formation of amidate V from IV was small compared to the overall enthalpy change for the decomposition. The overall enthalpy change as determined by DTA was  $-15.7$  kcal./mole. Analysis of the rate data obtained from DTA gave results comparable to those obtained by conventional techniques for the formation of dipolar ion intermediate IV from III ( $E_a = 29.8$  kcal./mole).

Reaction of diphenylphosphinyl azide (VI), diethyl phosphorazidate (I) or di-n-butyl phosphorazidate (LIX) with N,N-dimethyl-2-methylpropenylamine (XLIX) gave the corresponding N'-phosphorylated amidines LXIa-c in high yield.



A dipolar ion formed by the decomposition of a triazoline intermediate was postulated on the basis of the appearance of a band in the infrared spectrum at  $2100\text{ cm}^{-1}$  characteristic of  $\text{R}-\text{N}_2^+$ .<sup>88</sup> Unfortunately a triazoline intermediate could not be isolated from this chemical transformation.

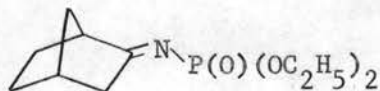
Diethyl phosphorazidate (I) reacted with norbornylene (II) to give diethyl (3a,4,5,6,7,7a)-hexahydro-4-7-methano-1H-benzotriazol-1-yl)-phosphonate



Triazoline III was obtained as a residual product by distillation at 0.1 mm. of the unreacted starting materials. The nuclear magnetic resonance (NMR) (Plate I) and infrared (IR) (Plate VII) spectra show the presence of only traces of starting materials, azide [NMR (Plate II), IR (Plate VIII)] and norbornylene (II).

Important evidence for the structure of triazoline III was afforded by NMR analysis (Plate I) which shows an AB quartet centered at  $\delta$  4.10 ( $J=8.5$  c.p.s.) and absorptions at  $\delta$  2.5 and 2.65 which are assigned to the non-equivalent C-4, C-7 bridgehead protons. The AB quartet at  $\delta$  4.01 is assigned to the C-3<sub>a</sub>, C-7<sub>a</sub> protons of triazoline III. Absorption at  $\delta$  2.61 and 2.73 in the NMR spectrum of the triazoline XX prepared from phenyl azide and norbornylene (II), is similar for the C-4, C-7 bridgehead protons. Infrared (Plate VII) absorption at  $6.6\mu$  is assigned to the N=N absorption. A band at  $7.88$  for P $\rightarrow$ O is characteristic of compounds containing this functional group.

When triazoline III was heated in boiling toluene for 3 hours a stoichiometric amount of nitrogen was lost with concomitant formation of diethyl 2-norbornylidenephosphoramidate (V) (90% yield) as the only product isolated in this reaction. Photolysis of III in Skellysolve-F resulted in the production of unidentified polymer (tar) and unreacted starting material.

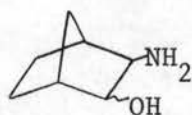


V

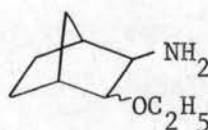


Amidate V was partially identified by its NMR spectrum (Plate III) and IR spectrum (Plate IX). The NMR spectrum (Plate III) of V contains peaks for the nonequivalent C-2, C-5 protons at  $\delta$  2.5 and 2.65, respectively. Similarly a doublet is observed ( $\delta$  2.85 and 3.10) in the same solvent for the 2,4-DNP of norcamphor, a close model compound. The AB quartet at  $\delta$  4.10 is no longer present in the spectrum of V. The IR spectrum (Plate IX) does not show absorption near  $3\mu$  (N-H) or at  $6.6\mu$  but strong bonds are visible at  $5.98\mu$  (C=N) and  $7.94\mu$  (P  $\rightarrow$  O). Hydrolysis of amidate V with 10% HCl gave ammonia, phosphoric acid and norcamphor which was isolated at its 2,4-DNP. Norcamphor was identified by mixture melting point of its 2,4-DNP with an authentic sample and comparison of the IR spectra.

Other evidence for the structure of triazoline III was afforded by the attempted reduction of III with Raney nickel in ethanol. Elemental analysis of the distilled reaction product after treatment with 10% boiling HCl, suggested a mixture of amino alcohol LXII and ethoxy amine LXIII.



LXII



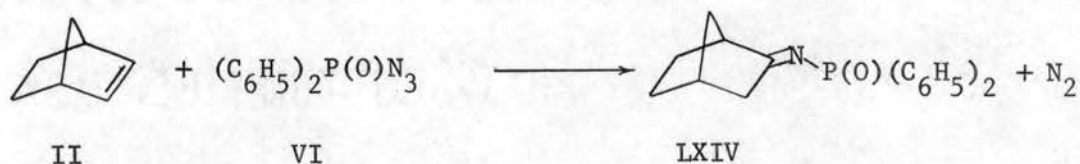
LXIII

Reactions of triazolines of this type are known to occur with nucleophiles.<sup>2</sup> It was suspected that the Raney nickel-ethanol reduction mixture promoted the surface-catalyzed decomposition of the triazoline III to an intermediate such as IV. Reaction of the latter with ethanol or water present in small amounts would give the observed products LXII and LXIII

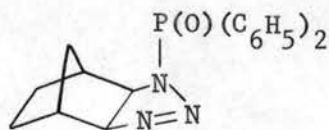
after hydrolysis. That an ionic intermediate IV might be formed was supported by the fact that a band at  $2100\text{ cm.}^{-1}$  (see Plate XV) in the IR was noticed during an attempted work-up of a reaction mixture (containing III) by column chromatography on alumina. The decomposition of III was apparently catalyzed by the alumina.

Reactions of diphenylphosphinyl azide (VI) with cyclohexene, diphenyl acetylene and butadiene were attempted. No identifiable products other than starting materials were isolated from these reaction mixtures. It was concluded that this type of azide required a more reactive substrate such as norbornylene (II) for reaction. It has been demonstrated by Looker<sup>54</sup> that reactions of azides such as tropylium azide with acetylenes occur only slowly with poor yield of products.

The reaction of diphenylphosphinyl azide with norbornylene at  $85\text{--}90^\circ$  gave only amide LXIV in moderate yield (68%). The reaction was slow, requiring more than 24 hours for azide absorption

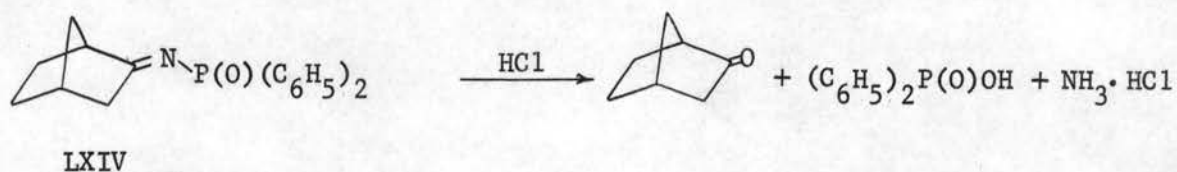


at  $4.7\mu$  in the IR spectrum to disappear. A triazoline intermediate such as LXV could not be detected by instrumental methods. Apparently the required reaction temperature may be sufficient to decompose the triazoline.



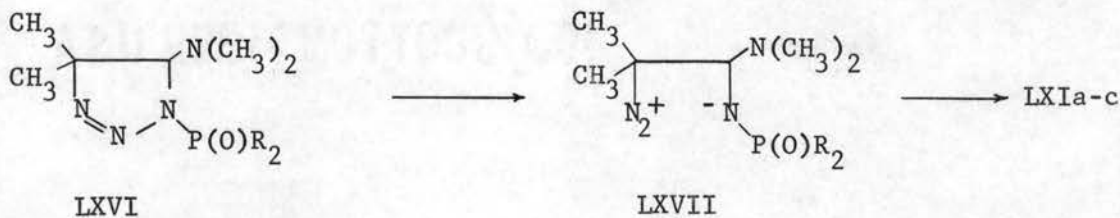
LXV

2-Norbornylidene-P,P-diphenylphosphinic amide (LXIV), the only product isolated in this reaction, was characterized by hydrolysis



with dilute HCl to norcamphor, (identified as its 2,4-DNP), diphenylphosphinic acid (quantitative yield) and ammonia which was identified by classic technique. The IR spectrum of amide LXIV (Plate X) contains peaks at  $5.97 \mu$  (C=N) and at 8.26 and 8.36 (doublet for P  $\rightarrow$  O).

Formation of amidines LXIa-c resulted from reaction of phosphoryl azides I and LX and phosphinyl azide VI with N,N-dimethyl-2-methylpropylamine (XLIX).<sup>13</sup> The mechanism for this transformation is thought to involve a triazolone intermediate such as LXVI which could decompose to a dipolar ion such as LXVII.

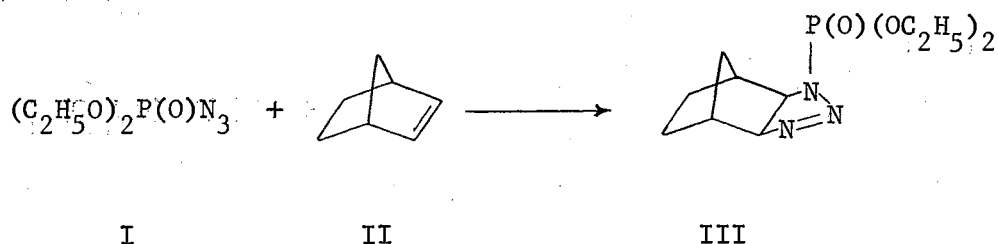


Evidence for such an ion as LXVII was afforded by IR analysis of the reaction mixture (see Plate XVI), which showed absorption at  $2100 \text{ cm.}^{-1}$  characteristic of  $\text{R-N}_2^+$  in aliphatic diazonium systems.<sup>88</sup> This band appeared soon after the reactants were mixed, became moderately intense during the majority of the reaction period and disappeared shortly after the azide absorption disappeared. The appearance and disappearance of the IR band at  $2100 \text{ cm.}^{-1}$  suggests that the dipolar ion LXVII may be quite

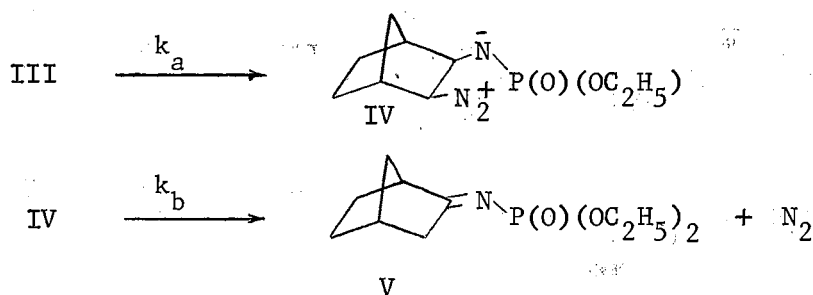
stable in the polar medium (the enamine was the solvent for the reaction) or that the ion formed and decomposed in consecutive reactions at comparable rates. Support for the latter is the fact that the reaction was not simple first, second, or third order as demonstrated in a single experiment where the rate of production of nitrogen was measured.

The reactions of phosphorus azides I, VI, and LX with enamine XLIX were carried out at room temperature (25-28<sup>o</sup>) with excess enamine XLIX as solvent. Characterization of the amidines LXIa and LXIb was accomplished by NMR and IR analysis and by complete hydrolysis to known compounds. The structure of amidine LXIc was based on the similarity of its NMR spectrum (Plate IV) and its IR spectrum with LXIa and LXIb. Treatment of LXIb with 10% HCl gave a quantitative yield of diphenylphosphinic acid (XIX). Ammonia and dimethylamine were obtained by distillation of the filtrate (made alkaline with NaOH) into 0.1N HCl. Separation of dimethylamine hydrochloride and ammonium chloride, which were identified by comparison of IR spectra, was accomplished by extraction with methylene chloride, ammonium chloride being completely insoluble. Isobutyric acid was identified by comparison of the IR spectrum of the distillate of the benzene extract from the acidified hydrolyzate with an authentic sample. The NMR spectrum of LXIb (Plate V) shows absorption at  $\delta$  1.14 (doublet for the C-methyl groups),  $\delta$  3.07 (singlet for the N-methyl groups) and  $\delta$  3.07 (heptet for the tertiary proton). The IR spectrum of LXIb (Plate XII) shows absorption at 6.25  $\mu$  (C=N) and 7.82  $\mu$  (P  $\rightarrow$  O). Hydrolysis of amidine LXIa by the same procedure gave ammonia, dimethylamine, isobutyric acid and phosphoric acid which was identified as ammonium phosphomolybdate. The NMR spectrum of LXIa (Plate VI) and the IR spectrum (Plate XIII) show absorption similar to those of LXIb and LXIc.

The kinetics of formation of triazoline III and its decomposition were determined in order to elucidate the mechanism for the overall transformation. The determination of the overall order for the formation was achieved by the use of NMR to follow the disappearance of I and II and appearance of III.



Solutions of I and II in cyclohexane were thermostated at 25-35° and the reaction followed by UV. Since I and II show low absorption at 271 mμ, it was possible to obtain kinetic data, using the method of initial rates to calculate the activation energy ( $E_a$ ) and entropy of activation ( $\Delta S^*$ ). Kinetics for the decomposition of III were determined in various solvents by following the rate of evolution of nitrogen and by DTA.



The overall order for the transformation  $\text{I} + \text{II} \rightarrow \text{III}$  as determined by NMR was two. The reaction rate constant ( $k$ ) determined in carbontetrachloride at 55.8° was  $1.40 \times 10^{-3}$  l./mole-min. Several experiments performed by this method gave relatively constant values for the rate constant calculated at various times, corresponding to various concentrations

of III from the equation

$$k = \frac{\ln \left[ \frac{(C_{NB}/C_{NB}^0)(C_{PA}^0/C_{PA})}{t(C_{NB}^0 - C_{PA}^0)} \right]}{t(C_{NB}^0 - C_{PA}^0)}$$

where  $C_{NB}$  refers to the concentration of norbornylene (II) and  $C_{PA}$  refers to the concentration of azide I. The rate constants calculated from a consideration that the reaction might be simple first order or simple third order varied considerably more than those obtained for the assumption that the reaction was second order.

The rather large variation in the rate constants in some experiments (see Experimental section) was probably due to a major source of error inherent in the method itself. Several standard solutions of norbornylene (II) containing a known amount of benzene as an internal standard were analyzed by NMR to determine the accuracy of the determination of norbornylene (II). An average of 98.0% of the norbornylene in the standard solutions was found by this method. All of the values were less than the theoretical. Since the absorption for the AB quartet of the triazoline III at  $\delta$  4.01 overlaps the absorption for the methylene in the phosphoryl group, the formation of triazoline III could not be used to confirm the results. For the same reason and the fact that absorption for the norbornylene protons overlaps the methyl protons absorption in the phosphoryl group of the azide at  $\delta$  1.0, the concentration of azide ( $C_{PA}$ ) was calculated from the stoichiometry and the norbornylene concentration. This could account for all the observed variation in the second order rate constants.

Formation of triazoline III was also studied by the method of initial

rates,<sup>30</sup> the formation of triazoline being followed by change in the UV absorption at 271 m $\mu$  due to triazoline III. The method of initial rates is based on the approximation that for the first few percent of reaction, a plot of the concentration of products or reactants versus time is a straight line. The observed rate is then determined from the slope of this line. The reaction order is calculable by determining the reaction rate at different concentrations of the reactants and calculating  $n_i$  (the order of reaction with respect to the  $i^{\text{th}}$  component) from the following general equations.

Let

$x$  = the concentration of product

A, B, C... = Concentration of reactants A, B, C...

Then:

$$\frac{dx}{dt} = kA^{n_a}B^{n_b}C^{n_c} \dots$$

if we determine  $(dx/dt)_1$  at concentration

$B_1$  and  $(dx/dt)_2$  at concentration

$B_2$  while holding the concentration of A, C ... constant, we

can determine  $n_b$  by dividing  $(dx/dt)_1 = kA^{n_a}B_1^{n_b} \dots$

by  $(dx/dt)_2 = kA^{n_a}B_2^{n_b} \dots$

$$n_b = \frac{\ln(dx/dt)_1 - \ln(dx/dt)_2}{\ln B_1 - \ln B_2}$$

The reaction rate constant can be calculated from the observed reaction rate and the initial concentration of reactants.

The order of reaction with respect to azide I as determined by this method was 1.04. Table II summarizes the data obtained by this method

for  $k$  at various temperatures. Figure 1 is the Arrhenius plot of these data. The energy of activation ( $E_a$ ) was calculated from the slope of the Arrhenius plot and  $\Delta S^*$  from transition state theory.

TABLE II  
RATE OF FORMATION OF TRIAZOLINE III  
BY ULTRAVIOLET METHOD

RUN NO.	TEMPERATURE $\pm 0.02^\circ\text{C}$	TOTAL CHANGE IN ABSORBANCE	$\Delta a / \Delta t$	$10^5 k$ (1/mole-min.)	$\ln k$
1	25.00	1.40	0.0265	1.52	-11.10
2	25.00	0.69	0.0033	1.52	-11.10
3	30.00	0.98	0.034	1.95	-10.85
4	34.90	1.36	0.064	3.66	-10.22

$E_a = 15.3 \text{ kcal./mole}$   
 $\Delta S^* = -27.4 \text{ e.}$

That the change in absorbance in the UV for the appearance of triazoline III during the reaction is affected very little by the change in absorption due to the disappearance of azide (I) can be seen from Plate XV and Plate XVI, presenting the UV spectra of I and III, respectively. At  $271 \text{ m}\mu$  triazoline III has an extinction coefficient of  $1.161 \times 10^3$  and that for azide is less than 10.

The entropy of activation (27.4 e.u.) for this reaction agrees with the values reported for the formation of triazoline XX ( $\Delta S^* = -31 \text{ e.u.}$ ) from phenyl azide and norbornylene (II).<sup>70</sup> On this basis a transition



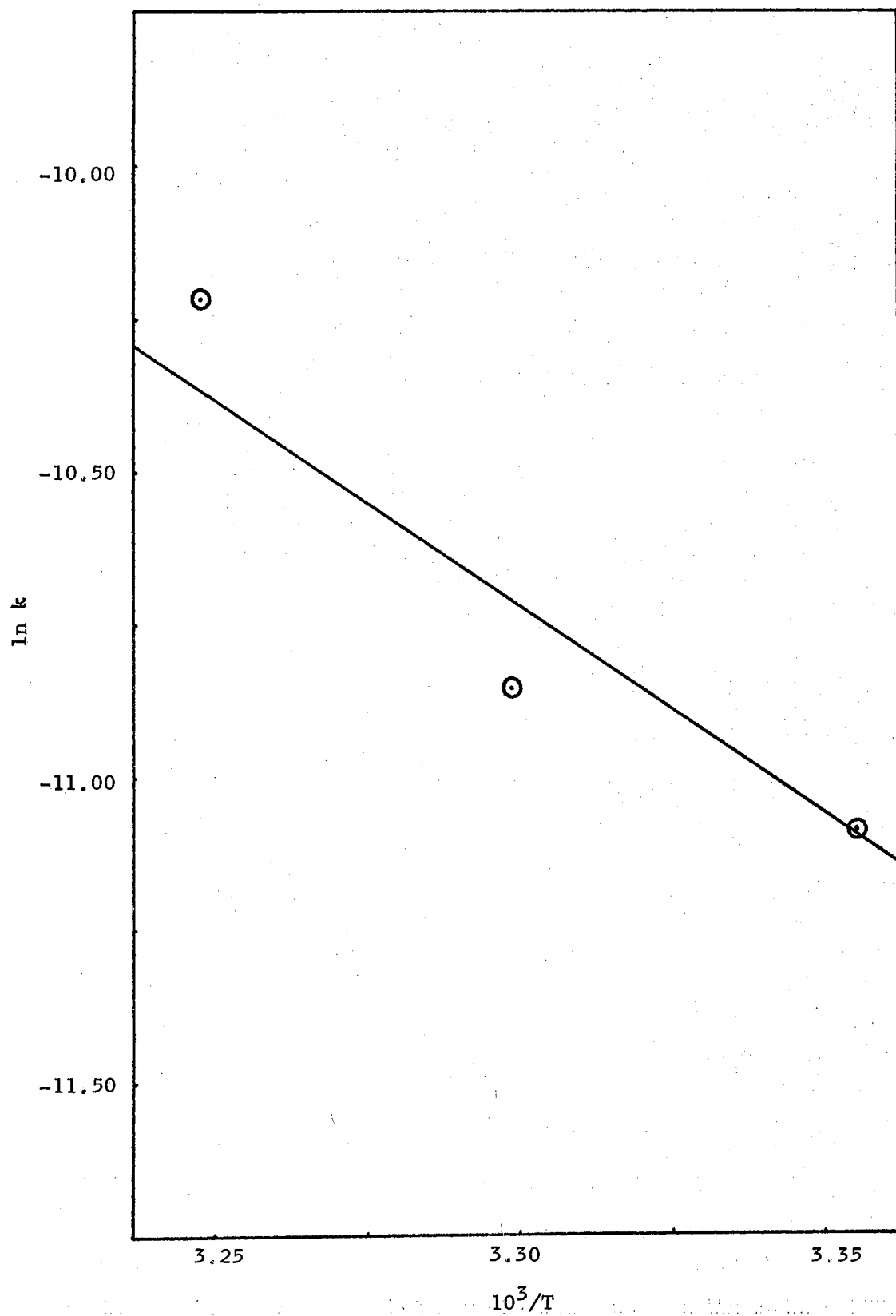
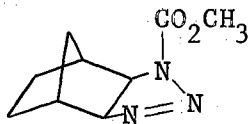


Figure 1. Arrhenius Plot for the Formation of Triazoline III.

state LIX, similar to that proposed by Scheiner<sup>70</sup> could be operative, in this reaction for the concerted 1,3-dipolar addition of azide I to norbornylene (II). Oehlschlager and Zalkow<sup>63</sup> reported that  $\Delta S^* = -31$  e.u. for the formation of triazoline XXVIII

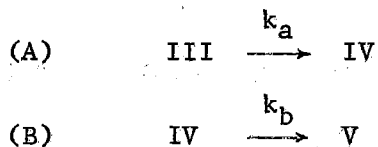


XXVIII

also in good agreement with these data. Triazoline XXVIII was also characterized by NMR since it could not be isolated in pure form because of its instability.

Kinetic data for the decomposition of triazoline III were accessible by the classic approach, i.e., following the rate of nitrogen evolution and also by the thermal method, DTA. The apparatus used to measure the rate of nitrogen evolution is shown schematically in Figure 2; Plate XX is a photograph of this apparatus. The technique is outlined in the Experimental section.

Attempts to fit the data for the rate of nitrogen evolution to simple first, second or third order rate laws gave large deviation in all cases. However, values calculated for  $k_a$  were found to be constant if two first order consecutive reactions were assumed.



The value for  $k_b$  as well as  $E_a$  and  $\Delta S^*$  for reaction (B) were determined by this method.

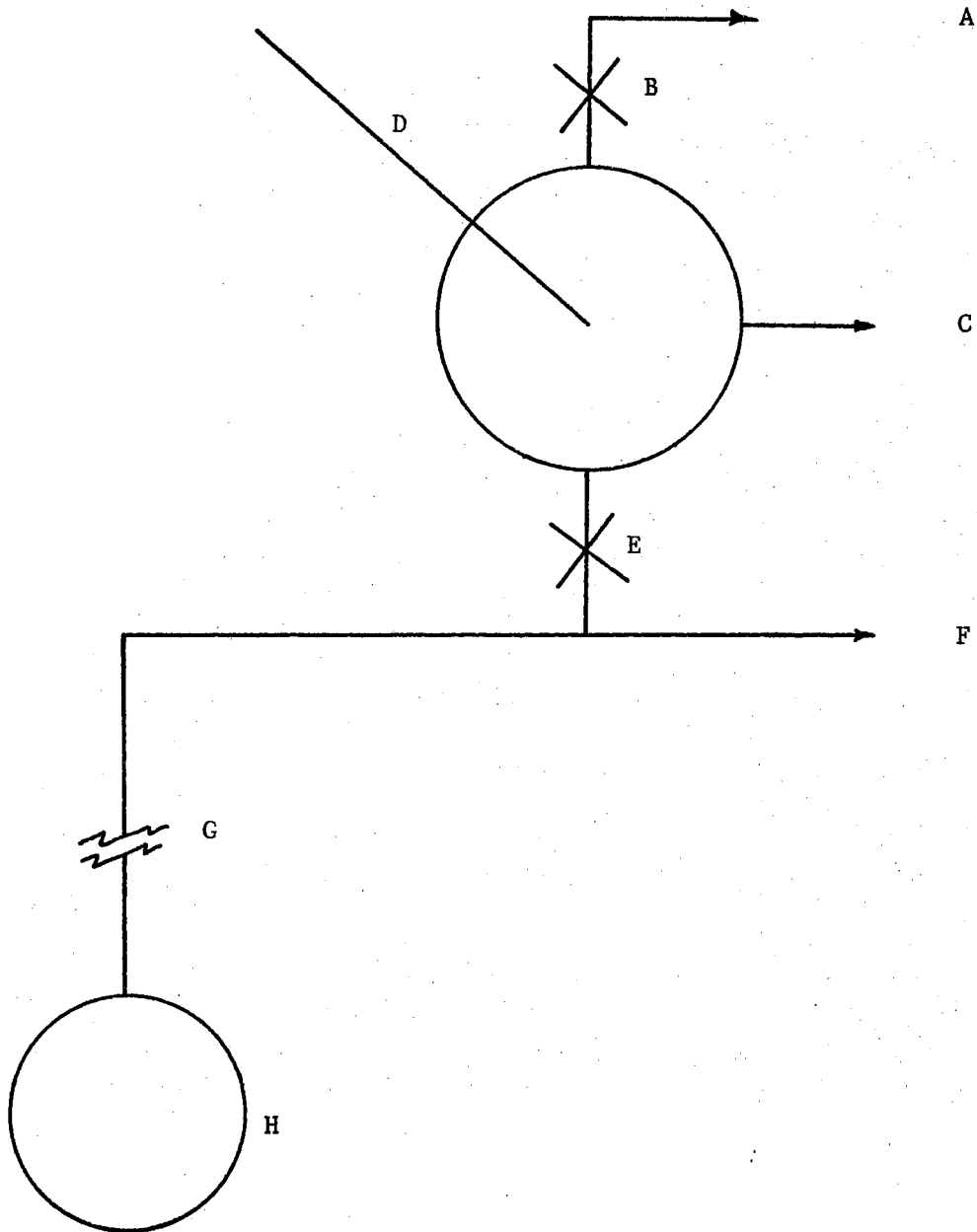


Figure 2. Apparatus for Measurement of Nitrogen Evolved by Conventional Method: A, to Vacuum Pump; B, Stopcock; C, to Manometer to Measure Nitrogen Pressure; D, Evacuated Bulb with Thermometer; E, Stopcock to Allow Nitrogen Produced to Enter D; F, to Manometer to Monitor Reaction System Pressure; G, Condenser; H, Reaction Flask.

Formulae for calculation of rate constants  $k_a$  and  $k_b$  were derived as follows. See Benson<sup>70</sup> and Rodiguin<sup>54</sup> for a complete discussion of first order consecutive reactions. In order to simplify the equations,

let

$A_0$  = concentration of triazoline III initially

$A$  = concentration of triazoline III at time  $t$

$B_0$  = concentration of dipolar ion IV initially

$B$  = concentration of dipolar ion IV at time  $t$

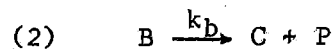
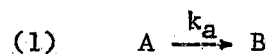
$C_0$  = concentration of nitrogen initially

$C$  = concentration of nitrogen at time  $t$

$P_0$  = concentration of amidate V initially

$P$  = concentration of amidate V at time  $t$

Then for the reaction



We have,

$$(3) \quad \frac{dA}{dt} = -k_a A$$

$$(4) \quad \frac{dB}{dt} = k_a A - k_b B$$

$$(5) \quad \frac{dC}{dt} = \frac{dP}{dt} = k_b B$$

Equation 3 can be integrated directly using initial conditions

$$\int_{A_0}^A d \ln A = \int_0^t -k_a dt$$

to give

$$(6) \quad A = A_0 e^{-k_a t}$$

Substituting this value for A into equation (4) we have

$$(7) \quad \frac{dB}{dt} + k_b B = k_a A_0 e^{-k_a t}$$

which is a linear differential equation of first order, the general solution of which is

$$e^{-k_b t}$$

and the particular solution is

$$e^{-k_a t}$$

The total solution is a linear combination of the two.

$$(8) \quad B = a_1 e^{-k_b t} + a_2 e^{-k_a t}$$

Where  $a_1$  and  $a_2$  are constants to be determined from the initial conditions and the original equation (7). Substituting B from (8) into (5) we obtain

$$\begin{aligned} & \frac{d(a_1 e^{-k_b t} + a_2 e^{-k_a t})}{dt} + k_b (a_1 e^{-k_b t} + a_2 e^{-k_a t}) \\ & = k_a A_0 e^{-k_a t} \end{aligned}$$

which gives

$$(9) \quad a_2 = \frac{k_a A_0}{k_b - k_a}$$

Substituting for  $a_2$  in (8) we have

$$B = a_1 e^{-k_b t} + \frac{k_a A_0}{k_b - k_a} e^{-k_a t}$$

Using the initial condition that at  $t = 0$ ,  $B = B_0$  we have

$$(10) \quad C_1 = B_0 - \frac{k_a A_0}{k_b - k_a}$$

Which on substitution into (8) yields

$$(11) \quad B = B_0 e^{-k_b t} + \frac{k_a A_0}{k_b - k_a} (e^{-k_a t} - e^{-k_b t})$$

Then from the stoichiometry

$$(12) \quad A + B + C = \text{constant} = A_0 + B_0 + C_0$$

$$C = A_0 + B_0 + C_0 - (A+B)$$

Substituting for A and B we have

$$(13) \quad C = A_0 + B_0 + C_0 - A_0 e^{-k_a t} - B_0 e^{-k_b t} - \frac{k_a}{k_b - k_a} (e^{-k_a t} - e^{-k_b t})$$

But  $B_0 = C_0 = 0$

So,

$$(14) \quad C/A_0 = 1 - e^{-k_a t} - \frac{k_a}{k_b - k_a} (e^{-k_a t} - e^{-k_b t})$$

If it is assumed that  $k_a < 0.1 k_b$  this equation reduces (rearranging)

to

$$(15) \quad \left(1 - \frac{C}{A_0}\right) = e^{-k_a t} \left[1 + \frac{k_a}{k_b - k_a}\right]$$

Solution of this equation at two different times ( $t_1$  and  $t_2$ ) corresponding to two different values of C ( $C_1$  and  $C_2$ ) gives,

$$(16) \quad k_a = \frac{1}{(t_2 - t_1)} \ln \left[ \frac{(1 - C_2/A_0)}{(1 - C_1/A_0)} \right]$$

Similar assumption for  $k_b$  and solving equation

(17) for  $k_b$  gives

$$(18) \quad k_b = \frac{k_a}{(1-C/A_0)(e^{+k_a t})-1} + k_a$$

Solution of these equations for  $k_a$  and  $k_b$  was accomplished with an IBM 1410 digital computer (see Experimental section for the Fortran IV program used for this calculation) by obtaining an initial value for  $k_a$  from equation (16) and  $k_b$  from equation (18) for each set of 15 points. These values were then substituted into equation (14) and the value of  $C/A_0$  that was calculated was compared to the experimental value of  $C/A_0$ . The value of  $k_b$  was then adjusted by the ratio  $(C/A_0)_{\text{calculated}}/(C/A_0)_{\text{experimental}}$  and a new value of  $C/A_0$  was determined from equation (14). This procedure was repeated until  $(C/A_0)_{\text{calculated}}/(C/A_0)_{\text{experimental}} = 1 \pm 0.004$ . The  $k_a$ 's and the  $k_b$ 's were then averaged, discarding doubtful values. Doubtful values of  $k_a$  were evaluated on the basis of whether the calculated value of  $k_a$  was far from the average value, and doubtful values of  $k_b$  were based on whether the  $(C/A_0)_{\text{calculated}}/(C/A_0)_{\text{experimental}}$  converged rapidly or  $k_b$  was negative. It should be noted that the value of  $k_b$  is highly dependent on the value calculated for  $k_a$ . An error of  $\pm 0.5$  mm. in the measurement of the pressure of nitrogen, assuming the value of  $A_0$  is correct, will cause an error of about  $\pm 0.04$  in  $k_a$  which in turn produces a considerable error in  $k_b$  since  $k_a$  appears in the exponential in equation (18).

Table III is a summary of the data obtained for  $k_a$  and  $k_b$  at various temperatures. Figure 3 is the Arrhenius plot of the  $k_a$  and Figure 4 is the Arrhenius plot for the  $k_b$ . Activation energies ( $E_a$ ) were determined

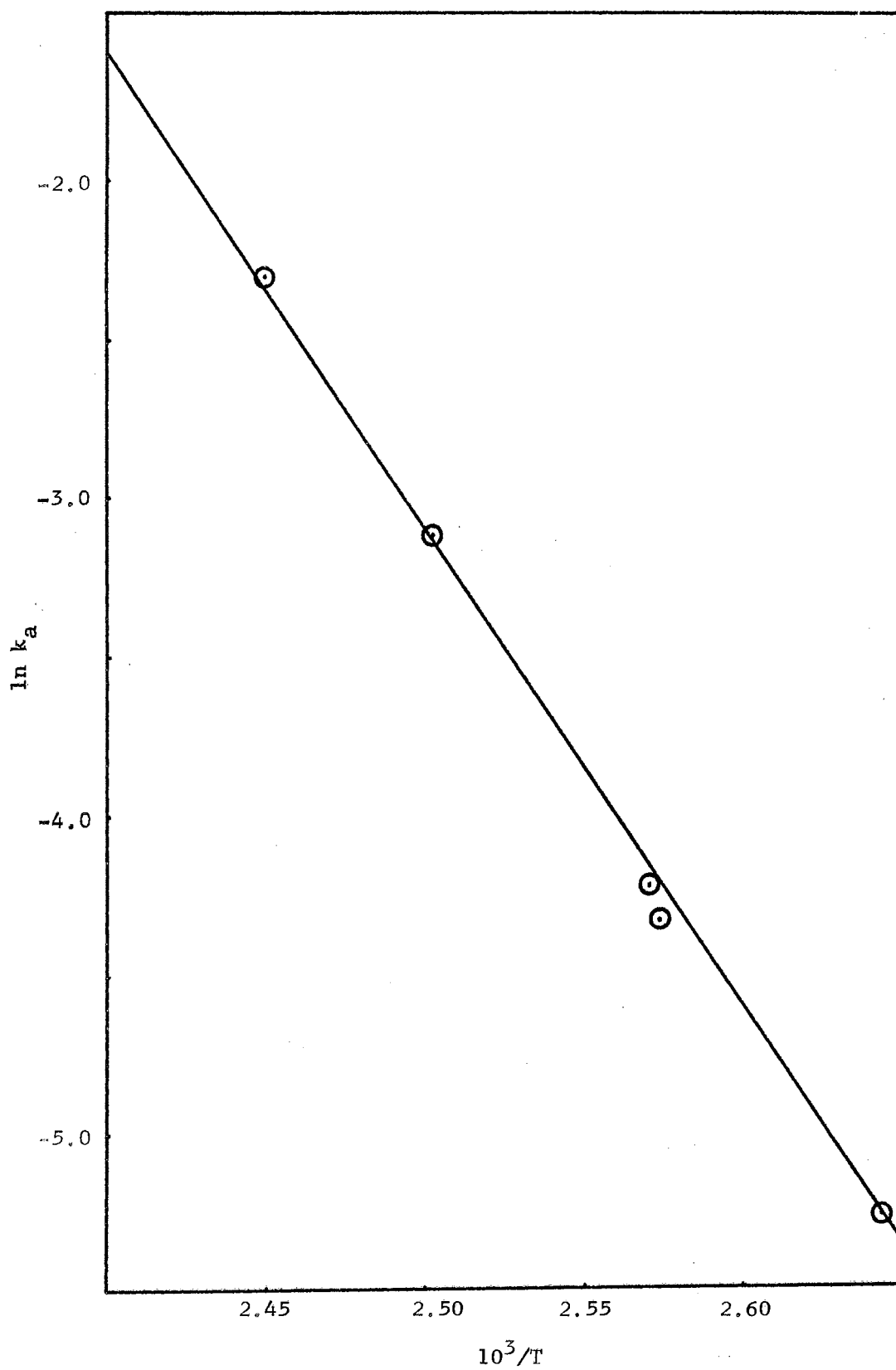


Figure 3. Arrhenius Plot of  $k_a$  for the Decomposition of Triazoline III.



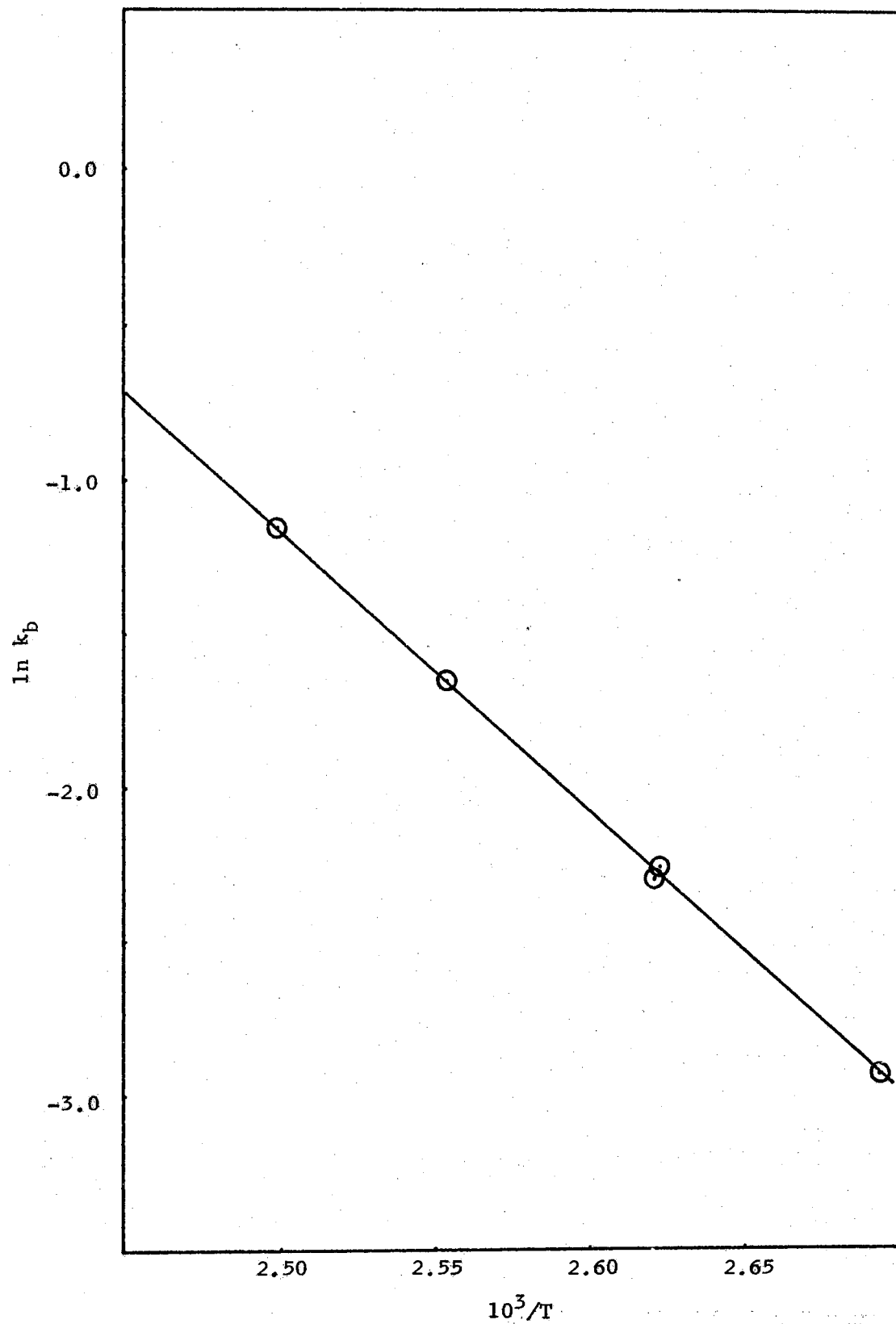


Figure 4. Arrhenius Plot for the Decomposition of the Dipolar Intermediate IV.

from the slopes of these curves. Values for  $\Delta S^*$  were calculated from transition state theory<sup>70</sup> which gives

$$\Delta S^* = R \ln \frac{hA}{kT}$$

where R is the gas constant, k is Boltzman's constant, h is Planck's constant and A is the Arrhenius preexponential factor determined from the intercept in the  $1/T$  vs  $\ln k$  plots (Figures 3 and 4).

TABLE III

TEMPERATURE DEPENDENCE OF  $k_a$  AND  $k_b$  IN DIGLYME SOLVENT

TEMPERATURE °K	$10^2 k_a$ (min. <sup>-1</sup> )	$10 k_b$ (min. <sup>-1</sup> )
371.20	0.528	0.545
380.96	1.31	1.05
381.26	1.47	1.00
391.16	4.24	1.90
399.66	9.80	3.42
$E_a = 29.8$ kcal./mole		$E_a = 17.9$ kcal./mole
$A = 1.95 \times 10^{17}$		$A = 1.07 \times 10^{11}$
$\Delta S^* = 19.6$ e.u. (381.2°K.)		$\Delta S^* = -8.54$ e.u. (381.2°K.)

Solvent effects on the rate constants ( $k_a$  and  $k_b$ ) were determined by measuring the rate of nitrogen evolution in solvents having different dielectric constants (different polarities). Table IV summarizes the

data obtained at 381.2°K. in toluene, diglyme and benzonitrite.

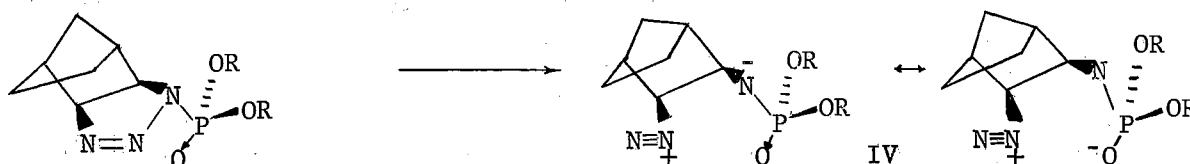
TABLE IV

SOLVENT DEPENDENCE OF RATE CONSTANTS AT 381.2±0.1°K

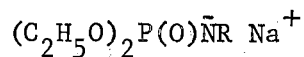
SOLVENT	$10^2 k_a$ (min. <sup>-1</sup> )	$10k_b$ (min. <sup>-1</sup> )
Toluene	0.873	0.236
Diglyme	1.471	1.00
Benzonitrile	3.04	1.80

From these results coupled with the fact that a band at 2100 cm.<sup>-1</sup> (see Plate XV), similar to that observed for the reaction of diethyl phosphorazidate (I) and enamine XLIX, appeared in the IR spectrum for the low-temperature surface-catalyzed decomposition of III, it is concluded that an ionic intermediate IV is formed in this reaction. Strong evidence is afforded by these data for a reaction mechanism involving two consecutive reactions. Also that the reaction rate constants ( $k_a$  and  $k_b$ ) were dependent on solvent polarity<sup>70</sup> supported this postulate (see Table IV).

Dipolar ion intermediates have been proposed by Fusco,<sup>32</sup> Huisgen,<sup>44</sup> Harrel,<sup>41</sup> Oehlschlager,<sup>63, 64</sup> Marsh,<sup>58, 57</sup> Berlin,<sup>13</sup> Munk,<sup>61</sup> and Logothetis<sup>53</sup> to explain the formation of the observed products in the decomposition of triazolone. In the system under discussion it is noteworthy that the N-substituted phosphoramidate portion of the dipolar ion IV

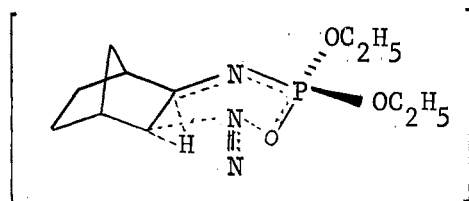


resembles the nitrogen analog of the Wittig reagents<sup>83</sup> LXVIII which are relatively stable.



LXVIII

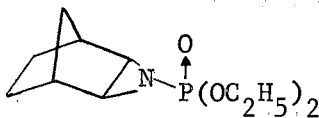
This fact suggests that a dipolar ion once formed could be stabilized by resonance delocalization involving d and p orbitals on phosphorus and nitrogen, respectively. Thus for formation of V from IV, a six-membered transition state LXIX may be involved. Simultaneous loss of nitrogen and hydride shift could occur as the incipient C=N bond is being generated.



LXIX

It should be recalled that P→O bonds in general are highly polarized having high bond-moments which could enhance the stability of LXIX.<sup>42</sup>

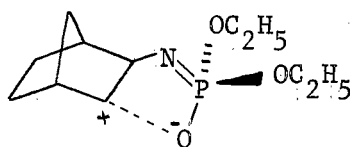
A mechanism of this type is consistent with all observations and is not unreasonable, considering the negative  $\Delta S^*$  (-8.54 e.u.) for the formation of products from the intermediate IV. It certainly explains why there is no evidence found for an aziridine such as LXX in the



LXX

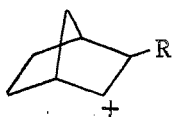
decomposition products of III. In analogy with the decomposition of the triazoline XXVIII from benzoyl azide (XVI) and norbornylene (II),<sup>44</sup> aziridine LXX would be expected if nitrogen were lost in a separate step. The

resulting ion could conceivably be stabilized by electrostatic interactions such as illustrated in LXXI.



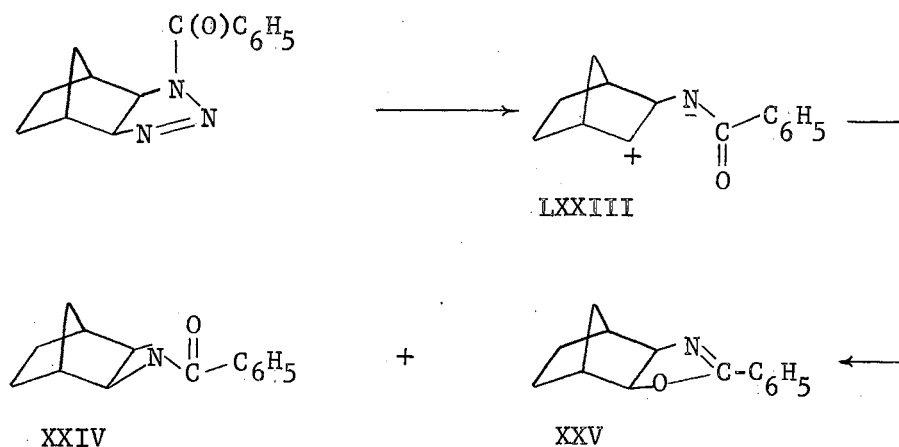
LXXI

If this were the case it is possible that ring closure (aziridine formation) could compete with hydride shift. An ion such as LXXII would be a



LXXII

necessary postulate if nitrogen were lost in a separate step. It is well known that carbonium ions of general structure LXXII undergo rapid rearrangements,<sup>15</sup> and no rearrangement products were found in the decomposition of III as evidenced by the good material balance. A carbonium ion such as LXXIII has been proposed by Huisgen<sup>44</sup> as part of the mechanism in the formation of aziridine XXIV and oxazoline XXV in the reaction of benzoyl azide (XVI) and norbornylene (II).



Stabilization of the transition state LXIX may be enhanced by the cis arrangement of the vicinal groups in the dipolar ion IV and the restricted rotation of the C-N bonds imposed by the norbornylene system.

Kinetics of the transformation III  $\rightarrow$  V determined by DTA indicated that the overall reaction was first order in III with an activation energy of 29 kcal./mole. Rate constant and the activation energy obtained agree very closely with  $k_a$  and  $E_a$  for the first of the two consecutive reactions (A), page 32 determined by measuring the rate of nitrogen evolution. This indicates that the enthalpy change for the second reaction (B) is small compared to that for the first reaction (A) on page 32. The enthalpy change for the first reaction was -16.2 kcal./mole. determined by comparing the area under the DTA curve with area under the DTA curve for the fusion of o-toluic acid. The enthalpy change for this transformation is 36.6 cal./g..

Apparatus employed to obtain DTA data for this transformation is shown schematically in Figure 5 and in a photograph in Plate XXI. This set up was quite simple and was assembled at a small cost compared to some of the more elegant apparatus such as calorimeters and thermogravimetric apparatus that have been used to obtain the same data. Calibration of the DTA apparatus is discussed in the Experimental section.

Equations for calculation of the first order rate constant  $k'$  for the decomposition of triazoline III by DTA were derived by Borchardt and Daniels<sup>18</sup> as follows.

Let:

$T_1$  = temperature of sample cell

$T_2$  = temperature of the reference cell

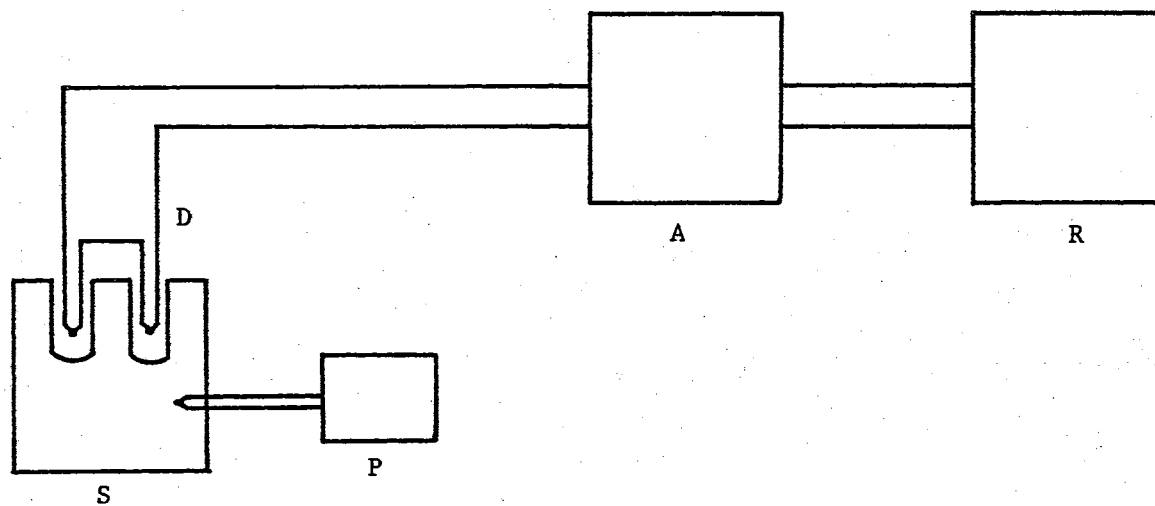


Figure 5. DTA Apparatus: S, Sample Block; P, Potentiometer with Thermocouple; D, Differential Thermocouple; A, D.C. Amplifier; R, Strip Chart Recorder.

- $T_3$  = temperature of the heating block  
 $K_r$  = heat transfer coefficient of the reference cell  
 $K_s$  = heat transfer coefficient of the sample cell  
 $C_{p,r}$  = heat capacity of reference  
 $C_{p,s}$  = heat capacity of sample  
 $dH$  = heat of reaction  
 $dt$  = time interval

Writing down the heat balance equation for sample and reference respectively we have

$$(19) \quad C_{p,s} dT_1 = dH + K_s (T_3 - T_1) dt$$

and

$$(20) \quad C_{p,r} dT_2 = K_s (T_3 - T_2) dt$$

If we assume:

1. Temperature of the cells is uniform.
2. Heat is transferred by conduction alone, and heat loss from thermocouple is small.
3.  $K_r = K_s = K$
4.  $C_{p,s} = C_{p,r} = C_p$

that is the solutions are dilute so that  $C_p$ /unit volume are approximately the same for sample and reference.

Equations (19) and (20) give



$$(21) \quad dH = C_p \Delta T + K \Delta T dt \quad \Delta T = (T_1 - T_2)$$

integrating over the range of t

$$\Delta H = C_p (\Delta T_\infty - \Delta T_0) + K \int_0^\infty \Delta T dt$$

$$\text{and } \Delta T_\infty = \Delta T_0 = 0$$

therefore,

$$(22) \quad \Delta H = K \int_0^\infty \Delta T dt$$

The integral is just the area under the DTA curve (A) (See Figure 6) so, equation (22) becomes:

$$\Delta H = KA$$

If it is assumed that the heat evolved in a small time interval (dt) is proportional to the number of moles (dn) reacting in that time,

$$dH \propto -dn$$

$$dH = - \frac{KA}{n_0} dn, \quad (KA/n_0 \text{ is the heat of reaction/mole})$$

We have,

$$(23) \quad \frac{-dn}{dt} = \frac{n_0}{KA} \left[ C_p \frac{d\Delta T}{dt} + K\Delta T \right]$$

which means that the reaction rate is proportional to  $d\Delta T/dt$  and  $T$  which are experimental quantities.

Recalling that

$$n = n_0 - \int_0^t \frac{dn}{dt} dt$$

equation (23) becomes,

$$n = n_0 - \frac{n_0}{KA} \left[ C_p \int_0^t \frac{d\Delta T}{dt} + K \int_0^t \Delta T dt \right]$$

(24)  $n = n_0 - \frac{n_0}{KA} [C_p \Delta T + Ka]$ , (a = shaded area under curve at time t in Figure 6)

but the reaction rate constant is

$$(25) \quad k' = -V^{x-1} \frac{dn/dt}{n^x}, \quad V = \text{volume of solution containing } n \text{ moles of reactant}$$

Substituting for k and rearranging

$$(26) \quad k' = \left[ \frac{KAV}{n_0} \right]^{x-1} \frac{C_p \frac{d\Delta T}{dt} + K \Delta T}{(K(A-a) - C_p \Delta T)^x}$$

where x is the reaction order.

Making the assumption that  $C_p d\Delta T/dt$  is small compared to  $K \Delta T$  and  $C_p \Delta T$  is small compared to  $K(A-a)$  equation (26) simplifies to equation (27) for first order reactions.

$$(27) \quad k' = \frac{\Delta T}{(A-a)}$$

A typical DTA experimental curve for the decomposition of III is shown in Figure 6, which is the curve after it had been retraced on small coordinate paper.

Since the method employed here did not utilize stirred cells as did Borchardt and Daniels,<sup>18</sup> the reaction of N,N-dimethylaniline and ethyl iodide was followed by DTA and the data compared to those of Borchardt and Daniels<sup>18</sup> (conventional method). Figure 7 shows the good agreement between

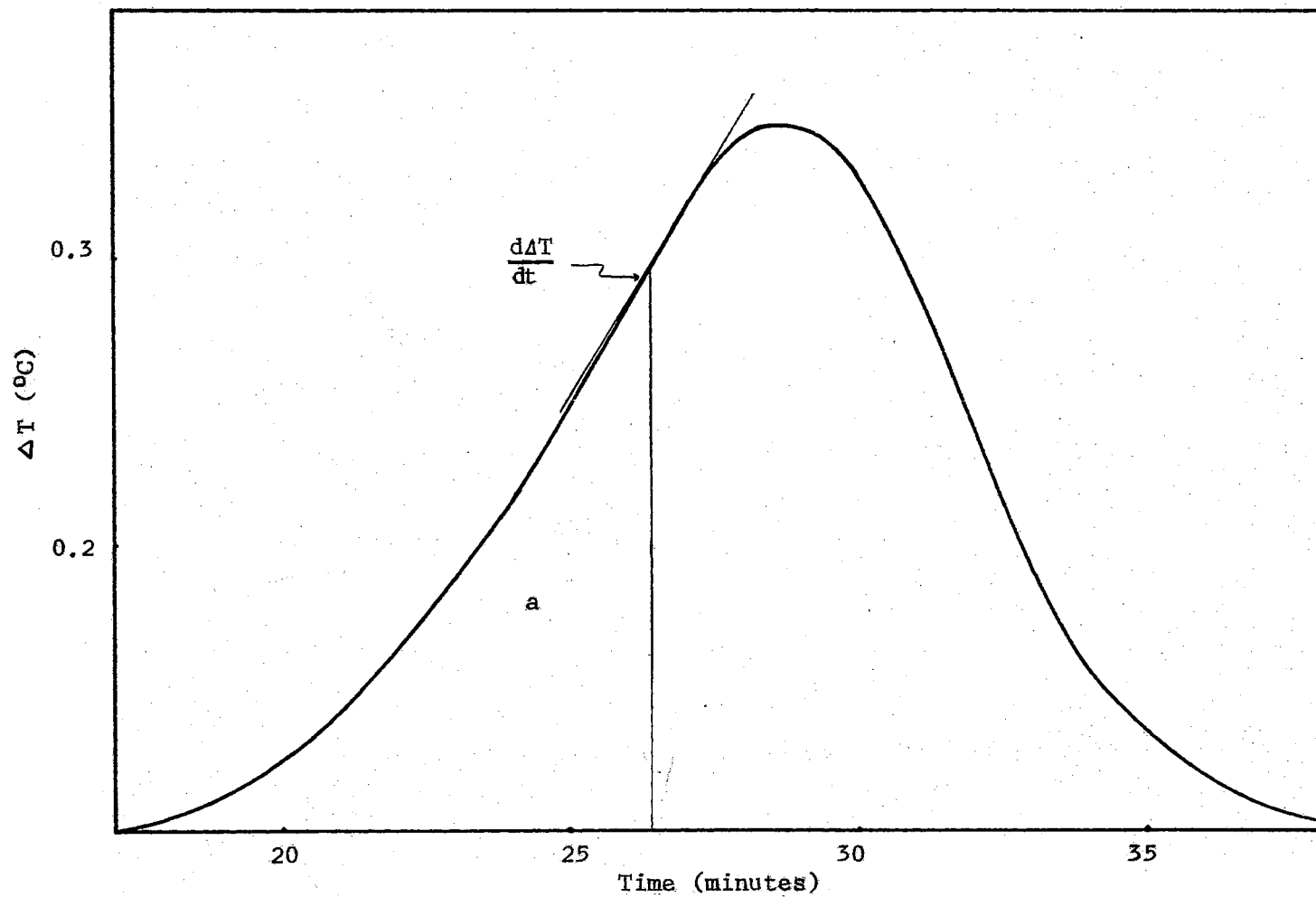


Figure 6. DTA Curve for the Decomposition of Triazoline III.

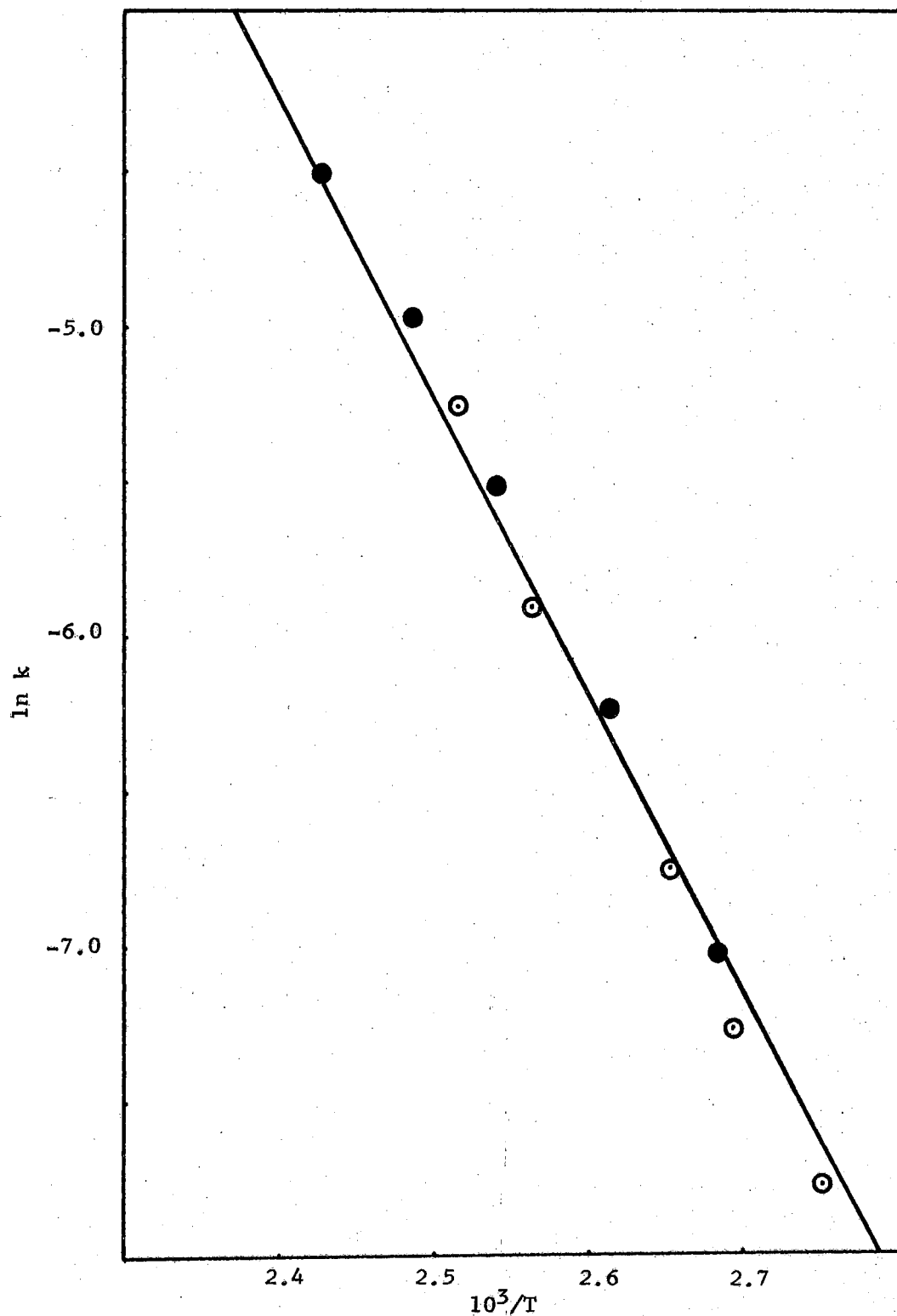


Figure 7. Arrhenius plot for the reaction of N,N-dimethylaniline with ethyl iodide. Solid line are data by Moelwyn-Hughes,<sup>60</sup> ○ are data by Borchardt and Daniels,<sup>18</sup> ● are data obtained in the present work.

these methods. Such agreement indicated that when small cells are employed stirring is apparently not necessary to be certain that the temperature of the cells is uniform.

Figure 8 is an Arrhenius plot of the data from DTA of the decomposition of III. The data were calculated from equation (27). Figure 9 is a comparison of the Arrhenius plot of the data for  $k_a$  obtained from nitrogen evolution and  $k'$  by DTA.

That such close agreement is obtained points out the utility of DTA as a method for determining reaction kinetics. The only requirements for the use of DTA for such determinations are that the reaction must be endothermic or exothermic, the reaction must be slow at some reasonable low temperature so that the reactants can be mixed without introducing large errors, and the reaction must go nearly to completion during the experiment. The reaction need not be simple [See equation (26)] because fractional orders ( $x$ ) can be easily determined by computer techniques. Some check on the data should be made, however, to be certain that complex reactions of the type discussed are not operative. If all of the above requirements are met (as they are by a great number of reactions in solution), DTA offers a simple and rapid method for the determination of reaction kinetics. It is surprising that DTA has not been applied more extensively since the time involved for collection and analysis of DTA data is about 1 day as compared to weeks for conventional methods.

Though substantial evidence has been collected in support of the decomposition of phosphorylated triazolines such as III via a dipolar ion IV to amidate V, it should be pointed out in summary that this is only one example of a general class of reactions involving phosphorylated

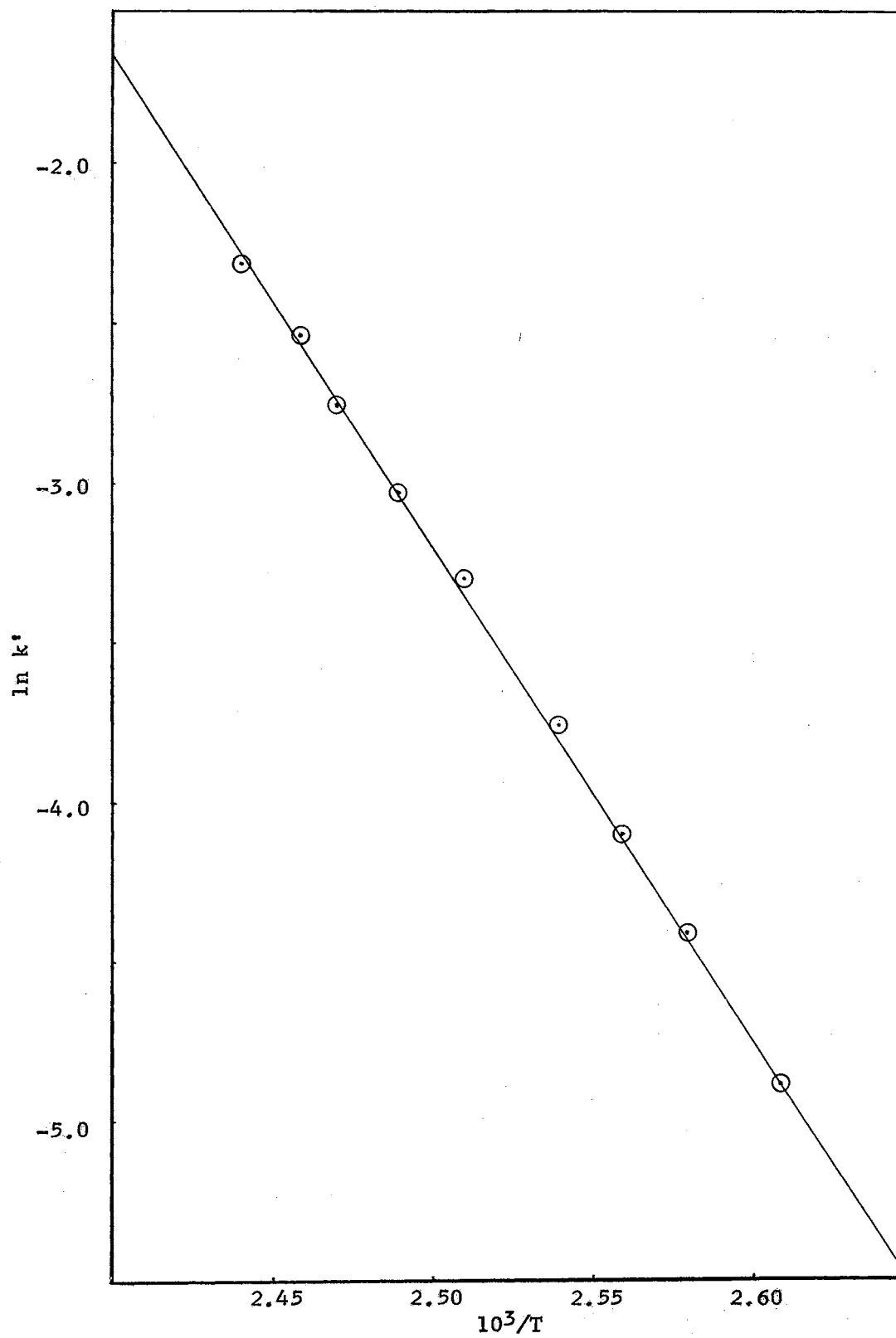


Figure 8. Arrhenius Plot of DTA Data for the Decomposition of Triazoline III.

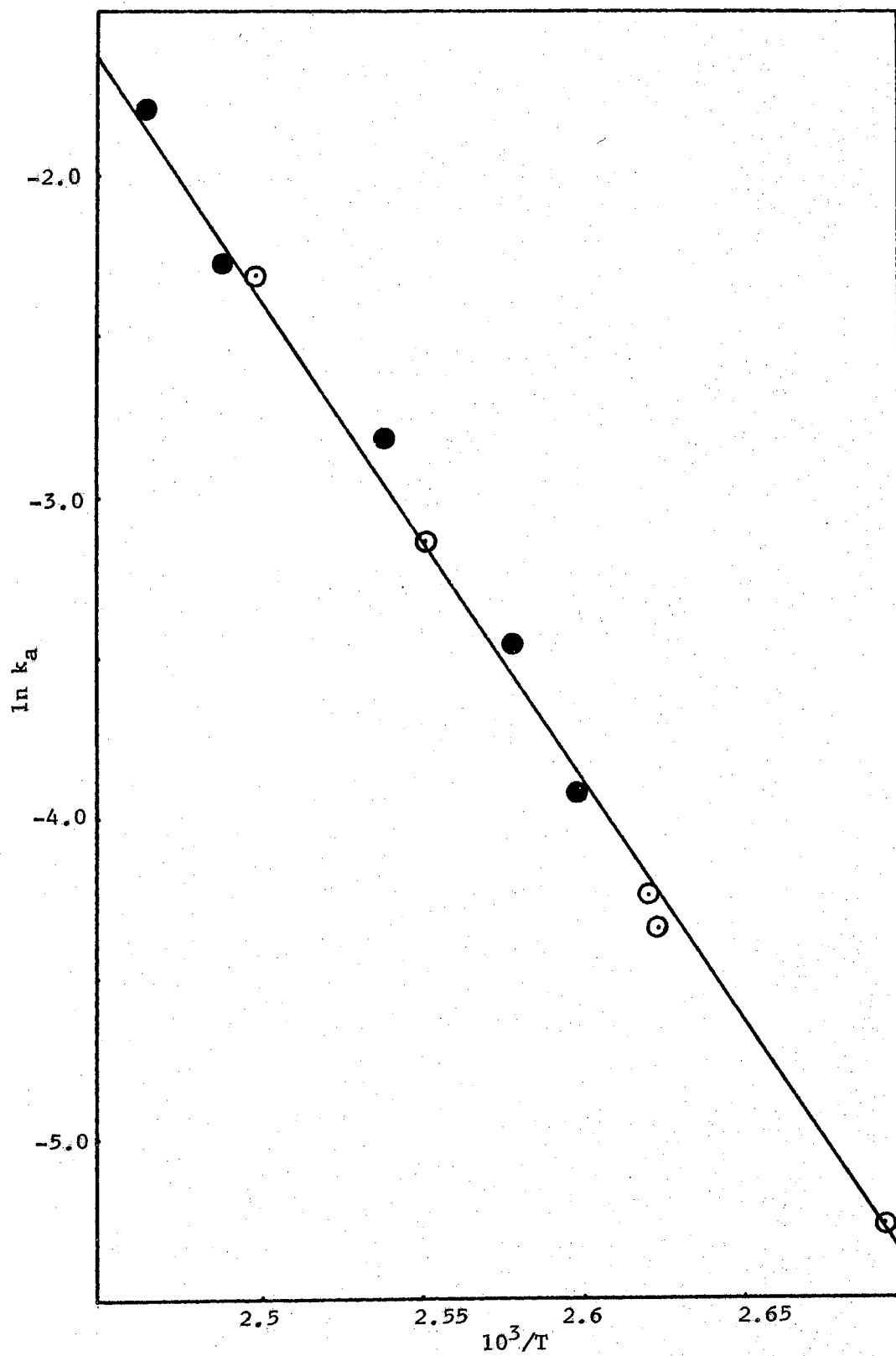


Figure 9. Arrhenius Plot for the Decomposition of Triazoline III;  $\odot$ , Data by Conventional Method,  $\bullet$  Data by DTA.

triazolines. This case and the data presented here suggest that phosphorylated triazolines may be formed (especially in the reaction of enamines with phosphorus azides) with other electron-rich olefins. Photolysis of phosphorylated triazolines may yield phosphorylated aziridines,<sup>69</sup> an unexplored method for the preparation of such compounds.

Differential thermal analysis of the decomposition of III afforded an excellent example of the applicability of DTA to solution kinetics. This reaction is one of many that could be studied without the disadvantages encountered in conventional methods. Complete analysis of reaction kinetics can often be achieved in less than 1 day by this simple technique where conventional approaches require weeks to obtain similar data that are perhaps no more precise.



## CHAPTER III

### EXPERIMENTAL a, b, c, d, e, f

Preparation of Diethyl Phosphorazidate (I). Diethyl phosphorazidate was prepared by the method of Scott, Riorden and Martin.<sup>74</sup> The best yields on the basis of several runs were obtained when freshly purified starting materials were used. Greater than 80% yield of product was realized when 65.0 g. (0.38 mole) of diethyl phosphorochloridate and 61.0 g. (0.94 mole) of sodium azide were allowed to react in reagent acetone (dried over type 5-A mole sieve) at 58° for 18 hours under a nitrogen atmosphere. Excess sodium azide and sodium chloride were filtered out and the product was distilled in vacuo. After solvent had been removed, only one fraction was collected, boiling at 40°/0.25 mm. (lit.<sup>1</sup>

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<sup>a</sup>All melting points are corrected and all boiling points are uncorrected.

<sup>b</sup>The infrared spectra were determined on Beckman IR-5 and IR-5A spectrometers as films on sodium chloride cells or as potassium bromide pellets.

<sup>c</sup>The nuclear magnetic resonance spectra were determined on a Varian A-60 high resolution spectrometer. Tetramethylsilane was used as an internal standard. Carbon tetrachloride was used as solvent unless otherwise specified.

<sup>d</sup>Gas chromatographic analyses were performed on an Aerograph Hy-Fi Model A-550 with a hydrogen flame ionization detector from Wilkens Instrument and Research, Inc., Walnut Creek, California.

<sup>e</sup>The ultraviolet spectra were determined on a Cary Model 14 Recording spectrometer and on a Beckman DK-1 recording spectrometer.

<sup>f</sup>The microanalyses were performed by Calbraith Laboratories, Knoxville, Tennessee.

76°/4.5 mm.); yield 60.3 g. (89.5%). The IR and NMR spectra (Plates II and VIII) indicate that the compound is quite pure.

Preparation of Diethyl (3a,4,5,6,7,7a-Hexahydro-4,7-methano-1H-benzotriazol-1-yl)phosphonate (III). Diethyl phosphorazidate (I) (10.0 g., 0.056 mole) and 20.0 g. (0.212 mole) of freshly distilled norbornylene (II) were placed in a 50-ml., round-bottom flask equipped with a condenser and a drying tube filled with type 5-A mole sieve. The reaction mixture was thermostated at 45° for 40 hours. During this time the extent of reaction was followed by observing the azide absorption in the 4.7  $\mu$  region of the IR. When azide absorption had nearly disappeared, excess norbornylene and unreacted azide were removed in vacuo, b.p. 45°/0.20 mm.; yield 13.9 g. (91%). IR and NMR spectra (Plates VII and I) of the residue (a straw-colored oil) indicated that there was little if any decomposition of the triazoline during the preparation. The IR spectrum shows no absorption at 3  $\mu$  for N-H and no absorption at 6  $\mu$  for C=N which is characteristic of the decomposition product III. NMR analysis shows the AB quartet centered at  $\delta$  4.10 ( $J = 8.5$  cps.) which has been assigned to the C-3a, C-7a protons of the triazoline III.<sup>12</sup> The nonequivalent C-4, C-7 bridgehead protons absorb at  $\delta$  2.5 and 2.65. Only a trace of norbornylene remained as indicated by the very weak absorption at  $\delta$  5.9 in the NMR.

Preparation of 2-Norbornylidene-P,P-Diphenylphosphinic Amide (LXIV).

Diphenylphosphinyl azide (10.0 g., 0.41 mole) (VI) and 20.0 g. (0.212 mole) of norbornylene were placed in a 100-ml. round-bottom flask equipped with a condenser, heating mantle and a type 5-A mole sieve drying tube. The reaction mixture was heated to 90° for 24 hours. A slow evolution of nitrogen was observed during the reaction period. IR analysis of the

reaction mixture after gas evolution had ceased showed no absorption in the  $4.7\mu$  region for azide. There was strong absorption at  $6.03\mu$  (C=N). Distillation of the reaction gave 9.0 g. (71% yield) of a dark oil (boiling range 185-190/1 mm.) that solidified to a glassy solid upon cooling. The IR spectra of samples taken before and after distillation were identical.

Anal. Calcd for  $C_{19}H_{20}ONP$ : C, 73.80; H, 6.54; N, 4.54; P, 10.02.

Found: C, 72.97; H, 6.71; N, 4.42; P, 10.03.

Several attempts were made at isolating possible intermediates leading to the amide LXIV in this reaction by running the experiment at lower temperatures and in polar and nonpolar solvents. None of these experiments provided evidence (i.e., disappearance of azide absorption in the IR) of reaction after periods as long as 100 hours. Perhaps reaction periods of greater than this would give the intermediates without decomposition at the lower temperatures.

Preparation of Diethyl-2-Norbornylidene phosphoramidate (V). Diethyl-2-norbornylidene phosphoramidate was prepared by decomposing the corresponding triazoline III prepared from norbornylene (II) and diethyl phosphorazidate (I) in boiling toluene. Azide I (10.0 g., 0.056 mole) and 13.2 g (0.14 mole) of norbornylene were allowed to react in apparatus previously described for 50 hours at  $40-46^{\circ}$ . Toluene (50 ml.) was then added and the resulting solution was heated to reflux. Nitrogen produced (1.25 l. over a period of about 3.5 hours) was collected by displacement of water in an inverted graduated cylinder (calcd. 1.26 l.). Solvent was then removed in vacuo and the product distilled to give 12.1 g. (88.4%) of V boiling at  $119^{\circ}/2.0$  mm.

Anal. Calcd. for  $C_{11}H_{20}O_3NP$ : C, 53.57; H, 8.22; N, 5.71; P, 12.63.

Found: C, 54.43; H, 8.43; N, 5.98.

IR examination (Plate IX) showed the absence of a peak at  $3\ \mu$  (N-H), strong absorption at  $5.99\ \mu$  (C=N) and strong absorption at  $7.88\ \mu$  (P $\rightarrow$ O). The NMR spectrum (Plate III) is consistent with the structure proposed, showing peaks for the nonequivalent bridgehead, C-3a and C-7a, protons at  $\delta$  2.5 and 2.65, respectively. Similarly a doublet is observed ( $\delta$  2.85 and 3.10) in the same solvent in the 2,4-DNP of norcamphor, a close model compound.

Hydrolysis of Diethyl-2-norbornylidenephosphoramidate (V). The amidate V (1.00 g., 0.004 mole) was placed in a 125-ml. Erlenmeyer flask with 10 ml. of 10% HCl. 2,4-Dinitrophenylhydrazene (1.0 g.) dissolved in a minimum amount of menthol was added and the resulting solution was heated on a steam bath for about 20 minutes and then set aside to cool. Crystals formed and were filtered out and dried, m.p.  $129^\circ$ . (1.0 g., 84.5%) A mixture melting point determination with an authentic sample of the 2,4-DNP of norcamphor, prepared by usual techniques,<sup>75</sup> was also  $129^\circ$ . The IR spectrum was identical to that of the authentic 2,4-DNP of norcamphor.

Phosphoric acid in the hydrolyzate was determined as follows: 4.00 g. of amidate V and 60 ml. of distilled water were added to a 200-ml. round-bottom flask equipped with a condenser, heating mantle and magnetic stirrer. Upon addition of 50 ml. of concentrated HCl the cloudy reaction mixture became light pink and emitted a distinct odor of norcamphor almost immediately. After boiling for about 2 hours, the entire reaction mixture was transferred quantitatively to a 200-ml. volumetric flask and diluted to volume when cold. To a 20-ml. aliquot was added enough 10% NaOH to bring the pH to about 3.0. The aliquot was then titrated potentiometrically

with 0.1102 N NaOH by the method of Blaedel and Meloche.<sup>16</sup> Two breaks in the pH curve were observed at pH 4.52 (0.78 ml. of titrant plus the 10% NaOH) and pH 7.52 (3.23 ml. of titrant). The total phosphoric acid content calculated from the difference in the two end points was 2.72 meq. (Theoretical was 3.36 meq.) 81% yield.

Phosphoric acid was determined qualitatively in the hydrolyzate with ammonium molybdate reagent. The test consisted of diluting about 10 drops of the hydrolyzate with 4 ml. of water and adding 3 drops of concentrated HNO<sub>3</sub> and 2 ml. of ammonium molybdate reagent. After boiling for about 1 minute, the solution became greenish yellow with the formation of a fine yellow precipitate. Ammonium molybdate reagent was prepared by dissolving 10.0 g. of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·24H<sub>2</sub>O in a mixture of 27 ml. of water and 15 ml. of concentrated NH<sub>4</sub>OH. This mixture was then added to 150 ml. of water to which 50 ml. of concentrated HNO<sub>3</sub> had been added.

Hydrolysis of 2-Norbornylidene-P,P-diphenylphosphinic Amide (XLIV).

To 4.1 g. (0.012 mole) of the amide XLIV, 50 ml. of 10% HCl was added. A precipitate of diphenylphosphinic acid formed after 1 hour of stirring at room temperature. After the precipitate (3.0 g., 0.011 mole) was filtered and dried, it melted at 183-189°. Recrystallization from methanol gave a pure sample of diphenylphosphinic acid, m.p. 192-194°. The filtrate, containing norcamphor and ammonia, was neutralized with 10% NaOH to a pH of 7.8 whereupon an oil separated and a strong amine odor was detected. Extraction with ether gave 2.0 g. of the oil (volatile) after removal of the ether. The 2,4-DNP of the oil was identical to the 2,4-DNP of norcamphor; yield, quantitative.

Preparation of N-(P,P-diphenylphosphinyl)-N',N'-dimethylisobutyryl-

amidine (LXIb). A 250-ml. Erlenmeyer flask was charged with 10.0 g. (0.041 mole) of diphenylphosphinyl azide and 78 ml. (0.58 mole) of N,N-dimethyl-2-methylpropenylamine. The reaction mixture was permitted to stand for 12 hours. During the reaction period, nitrogen gas was evolved at a steady rate. Crystals of product began to form after about 3 hours. A first crop of crystalline product (10.35 g., m.p. 132-138<sup>o</sup>), was filtered out. A second crop of crystals (1.23 g., m.p. 136-138<sup>o</sup>), was obtained by concentration of the filtrate to half of its original volume, cooling and filtering. Total yield of crude product, based on azide, was 90.0%. Recrystallization of a small sample for analysis from a 50:50 mixture of benzene and Skellysolve-F gave product with m.p. 137.5-9<sup>o</sup>.

Anal. Calcd. for C<sub>18</sub>H<sub>23</sub>ON<sub>2</sub>P: C, 68.80; H, 7.36; N, 8.91; P, 9.84;  
N.Eq. 314.4.

Found: C, 67.73; H, 7.22; N, 8.44; P, 9.63;  
N.Eq. 318.4.

Absorption in the IR (Plate XII) appeared at 6.25  $\mu$  (C=N), and at 7.84 (P  $\rightarrow$  O). NMR analysis (Plate V) showed signals at  $\delta$  1.14 (doublet) for the C-methyl groups,  $\delta$  3.07 (singlet) for the N-methyl groups and at  $\delta$  3.40 (heptet) for the tertiary hydrogen.

Preparation of N-(Diethylphosphoryl)-N',N'-dimethylisobutyramidine (LXIa). A 125 ml.-Erlenmeyer flask was charged with a 5.0 g. (0.028 mole) of diethyl phosphorazidate and 15 ml. (0.11 mole) of N,N-dimethyl-2-methylpropenylamine and let stand for 12 hours protected from moisture by a drying tube filled with 5-A mole sieve. During the reaction period a gas (nitrogen) was given off steadily. Fractionation of the light green viscous oil in vacuo, after evaporation of excess enamine, gave 5.88 g.

(0.024 mole) (83.9%) of product, boiling range 128-134<sup>o</sup>/1 mm. The wide boiling range was due to superheating of the distillation flask necessary to keep the distillate from condensing in the column.

Anal. Calcd. for C<sub>10</sub>H<sub>23</sub>O<sub>3</sub>N<sub>2</sub>P: C, 47.99; H, 9.26; N, 11.20; P, 12.38;  
N.Eq., 250.3.

Found: C, 48.27; H, 9.42; N, 10.98; P, 12.59;  
N.Eq., 254.3.

IR analysis (Plate XIII) shows strong absorption at 6.30  $\mu$  (C=N) and at 7.82 and 8.15 ( $P \rightarrow O$ ). NMR analysis (Plate VI) shows absorption at  $\delta$  1.18 (doublet) for C-methyl groups,  $\delta$  3.07 (singlet) for the N-methyl groups and at  $\delta$  3.40 (heptet) for the tertiary hydrogen.

Diphenylphosphinyl Azide. Generous samples of diphenylphosphinyl azide were donated by American Potash and Chemical Corp., Los Angeles, California, and were used without further purification. The IR spectrum of this compound (Plate XIV) showed strong absorption at 4.74  $\mu$  ( $-N_3$ ) and at 7.88 and 8.15  $\mu$  ( $P \rightarrow O$ ).

Preparation of N-(Di-n-butylphosphonyl)-N',N'-di-methylisobutyramidine (XIII). In the usual apparatus was placed 5.0 g. (0.024 mole) of di-n-butyl phosphorazidate and 15 ml. (0.11 mole) of N,N-dimethyl-2-methylpropenyl amine, and the mixture was allowed to stand 12 hours protected from moisture by a drying tube filled with type 5-A mole sieve. Again during the reaction period nitrogen was given off steadily. Fractionation of the straw-yellow viscous oil in vacuo, after evaporation of the excess enamine, gave 5.43 g. (0.018 mole, 74.2%) of product bp. 176/1.0 mm.

Anal. Calcd. for C<sub>14</sub>H<sub>31</sub>O<sub>3</sub>N<sub>2</sub>P: C, 54.98; H, 10.19; N, 9.15; P, 10.12;  
N.Eq., 306.4.

Found: C, 55.07; H, 10.20; N, 9.38; P, 10.17;  
N.Eq., 310.4.

IR (Plate XI) and NMR (Plate IV) spectra are consistent with the proposed structure and indicate the presence of only trace impurities.

N,N-Dimethyl-2-methylpropenylamine. Samples of this compound were obtained from Eastman Chemical Products, Inc., Kingsport, Tennessee; refractive index  $n_D^{20} = 1.4219$  (Reported<sup>26</sup> 1.4221). The samples were used without further purification.

Hydrolysis of N-(P,P-Diphenylphosphinyl)-N',N'-dimethylisobutyramidine.  
A 1.20-g. (0.00382 mole) sample of amidine XLIX was charged with 30 ml. of 10% HCl to a 50-ml. round-bottom flask equipped with a condenser, magnetic stirring apparatus and a heating mantle and heated to reflux for 3 hours. When 10% HCl was added, a clear solution resulted which became cloudy (precipitation of diphenylphosphinic acid) as the reaction progressed. Diphenylphosphinic acid, m.p. and mixed m.p. 193-194°, was filtered off and washed with acetone and air dried; yield, quantitative.

The colorless, odorless filtrate was then made alkaline with 10% NaOH and allowed to reflux for 12 hours. The residue was concentrated to about 1/3 of the original volume and finally dried by azeotropic distillation of the water with benzene. The solid obtained, a mixture of sodium isobutyrate and NaOH, was stirred in benzene and dry HCl gas was bubbled in until reaction ceased as evidenced by the fact that the reaction mixture began to cool. After removal of the NaCl by filtration and of the benzene in vacuo the residue (about 0.1 g.) had a distinct odor of isobutyric acid. IR and NMR spectra were identical to those of an authentic sample of isobutyric acid.



Analysis of N-(P,P-Diphenylphosphinyl)N',N'-dimethylisobutyramidine (LXIb) for Ammonia and Dimethylamine. A 1.000-g. (0.00318 mole) sample of LXIb was hydrolyzed with 50 ml. of 10% NCl as described previously. Ten percent NaOH (100 ml.) was added and the reaction flask was set up for simple distillation of the ammonia-water-dimethylamine mixture into 100 ml. of 0.1 N HCl solution. The distillation was stopped after about 2 hours when the distillate was no longer basic. Evaporation of the water and excess HCl gave 0.4200 g. (theoretical 0.4310 g.) of solid ammonium chloride and dimethylamine hydrochloride mixture; yield, 97.6%. The mixture was separated by extracting the solid with methylene chloride, ammonium chloride being completely insoluble. The NMR spectrum of the extract was identical with the NMR spectrum of an authentic sample of dimethylamine hydrochloride in methylene chloride. Ammonium chloride was identified by the fact that it gave off ammonia when treated with concentrated NaOH.

Gas Chromatographic Analysis of N-Phosphorylated Amidines.<sup>10</sup> Analyses were made on a 6-ft. by 1/8-inch column packed with Silicon 12, 30 on Chromosorb G. Retention times at 250° with flow rates of 28 cc./min. (N<sub>2</sub>) and 22 cc./min. (H<sub>2</sub>) were 20.7 minutes for N-(P,P-diphenylphosphinyl)-N',N'-dimethylisobutyramidine, 2.8 minutes for N-diethylphosphoryl-N',N'-dimethylisobutyramidine and 6.4 minutes for N-di-n-butyl-N',N'-isobutyramidine.

Attempted Reduction of Triazoline III with Raney Nickel. A 250-ml. centrifuge tube was charged with 20 g. (0.073 mole) of triazoline III that had been prepared from freshly distilled starting materials and 100 ml. of absolute ethanol. Raney nickel catalyst (RNC-28) (2.0 g.) that

had been carefully rinsed 3 times with 40-ml. portions of SD 3-A ethanol were then added. Upon addition of the catalyst a gas was evolved, apparently from the catalyst surface. The reaction flask was then placed on a Parr shaker and flushed 2 times to 50 psig. with hydrogen. The pressure was then adjusted to 50 psig. and restored to this pressure after each 10-psig. drop. Hydrogen uptake was rapid at first but stopped in less than 3 hours. A pressure of 50 psig. was maintained for an additional 8 hours during which time only a 2-psig. drop was recorded. The catalyst was filtered out, washed with two 50-ml. portions of ethanol, and discarded. The filtrate had no odor of ammonia. Distillation of the filtrate, after evaporation of solvent in vacuo, gave a main fraction (5.0 g.) boiling at 139°/3 mm. Several small fractions ( 0.5 g.), were also collected at lower and higher temperatures but were discarded. The fraction boiling at 139°/3 mm. was analyzed.

Found: C, 53.07; H, 8.88; N, 5.43; P, 11.55.

These analyses indicate that this compound is probably N-diethylphosphoryl-2-ethoxynorbornylamine contaminated with N-diethylphosphonyl-2-hydroxynorbornylamine.

Anal. Calcd. for  $C_{13}H_{26}O_3PN$ : C, 56.70; H, 9.53; N, 5.10; P, 11.30.

IR analysis shows presence of N-H, possibly O-H, and P-O. The NMR is similar to that of diethyl phosphorazidate.

The remaining portion (4.5 g.) of the fraction boiling at 139°/3 mm. was charged to a 50-ml., round-bottom flask to which 35 ml. of 10% HCl had been added. The resulting solution was boiled 10 hours. After being cooled and neutralized with 10% NaOH, the reaction mixture was extracted with four 100-ml. portions of ethyl ether. The extracts were

combined and evaporated to dryness. The oily residue was fractionated in vacuo to give a product, (0.8 g.) bp. 80°/20 mm.

Anal. Calcd. for C<sub>9</sub>H<sub>17</sub>NO (2-ethoxynorbornylamine LXIII):

C, 69.60; H, 11.06; N, 9.09

Found: C, 68.49; H, 11.30; N, 9.04.

IR analysis shows a broad doublet at 3.1  $\mu$  (N-H), medium absorption at 6.29  $\mu$  (N-H deformation) and doublet at 9  $\mu$  that could be C-N or C-O stretch. NMR analysis shows peaks at  $\delta$  1.10 (multiplet),  $\delta$  1.80 (multiplet),  $\delta$  2.94 (singlet) and  $\delta$  3.42 (multiplet).

Photolysis of Triazoline III. A 200-ml. round-bottom quartz flask equipped with a condenser and magnetic stirrer was charged with 15.4 g. (0.056 mole) of triazoline III, that had been prepared from freshly distilled starting materials, and 60 ml. of Skellysolve-F. The stirred reaction was irradiated with a 100-watt medium-pressure Hanovia mercury vapor lamp for 19 hours at 41°. The reaction mixture, which became dark with polymeric material forming on the surface of the reaction vessel, showed no apparent changes in the NMR or IR spectra during the reaction period. Attempts to separate possible products, that could not be detected by IR or NMR, by column chromatography on neutral alumina resulted in decomposition of the unreacted triazoline on the alumina surface to form amidate V. Several of the fractions from the column had absorption in the IR at 4.84  $\mu$  characteristic of R-N<sub>2</sub><sup>+</sup> (see Plate XV).

Procedure for Determination of the Kinetics of Formation of Triazoline III from Diethyl Phosphorazidate (I) and Norbornylene (II) by Ultraviolet Spectroscopy. The rate constant as a function of temperature for the formation of triazoline from diethyl phosphorazidate and norbornylene

was determined by the method of initial rates.<sup>30</sup> The procedure employed was similar to that described by Scheiner<sup>70</sup> to determine the rate constants for the formation of triazolines from norbornylene and substituted phenyl azides. For example, standard solutions of 1.949 molar azide and 6.937 molar norbornylene in cyclohexane were prepared and allowed to equilibrate at  $25.00 \pm 0.02^\circ$  for about 30 minutes. A 1-ml. sample of azide and a 2-ml. sample of the norbornylene solution were then mixed in a tightly stoppered, 3-ml. (1-cm.) quartz cuvette. The reaction mixture was then placed in the sample beam of a Cary Model 14 spectrometer. (The sample and reference compartments of the spectrometer were also thermostated at  $25.00 \pm 0.02^\circ$ .) A 3-ml. sample containing 1 ml. of the azide solution in cyclohexane was used in the reference beam. The reaction was then scanned at 271.7  $\mu$ , where the molar extinction coefficient was determined to be  $1.161 \times 10^3$  for triazoline III and less than 10 for azide I. After about 100 minutes, the change in absorbance was about 1.0 unit, corresponding to an extent of reaction of less than 1%. The slope of the straight line observed,  $\Delta$ absorbance/ $\Delta$ time, was then related to the reaction rate,  $d(\text{triazoline})/dt.$ , by multiplying by  $\epsilon^{-1}$ , and the rate constant was calculated from the initial concentrations of azide and norbornylene. The order of the reaction with respect to azide was found to be 1.04 (1.00 within experimental error) by varying the initial concentration of azide and calculating the rate.

Data obtained from the 4 runs by this procedure are tabulated in Table II. Figure 10 is a graph of these data. Figure 1 is the Arrhenius plot of these data. The activation energy was calculated directly from the slope of the Arrhenius plot.

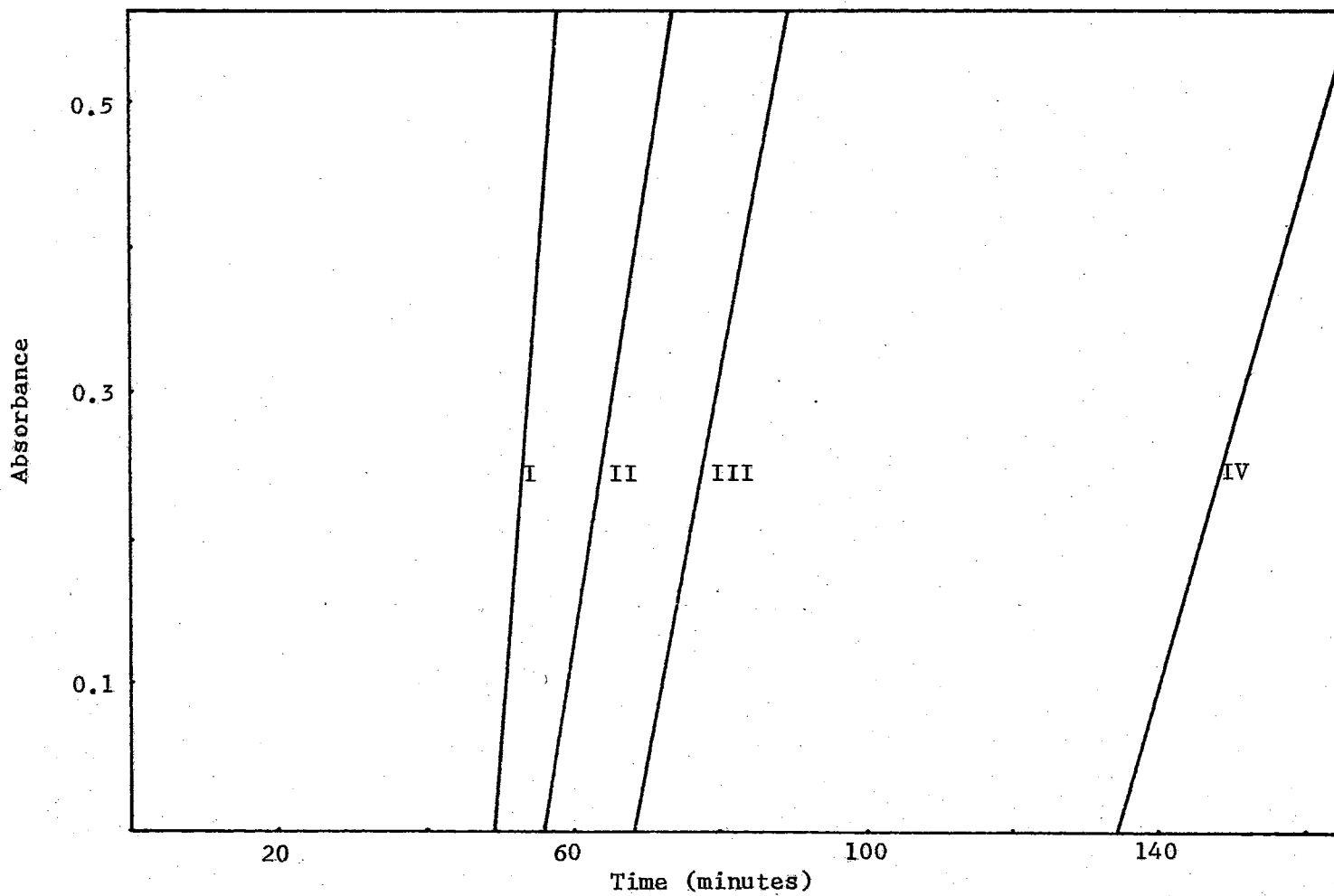


Figure 10. Rate of Formation by UV Method I, Run 1; II, Run 2; III, Run 3; IV, Run 4.

$$-E_a/RT = \ln k - \ln A$$

$$\text{Slope} = -E_a/R$$

The entropy of activation was calculated from transition state theory where the terms refer to classic descriptions.

$$\Delta S^* = R \ln \frac{Ah}{kT}$$

Procedure for Determination of Kinetics of Formation of Triazoline III from Diethyl Phosphorazidate (I) and Norbornylene (II) by NMR. The second order rate constant as a function of temperature in carbon tetrachloride was determined by allowing norbornylene and diethyl phosphorazidate to react at constant temperature for various periods of time and following the extent of reaction by determining the concentration of norbornylene and triazoline III with NMR using benzene as an internal standard. The rate constant at various times was calculated from the integrated rate equation.<sup>70</sup>

$$k = \frac{\ln [(C_{NB})/C_{NB}^0)(C_{PA}^0/C_{PA})]}{t (C_{NB}^0 - C_{PA}^0)}$$

where  $C_{NB}$  and  $C_{NB}^0$  denote the concentration of norbornylene at time  $t$  and the initial concentration of norbornylene respectively, and  $C_{PA}$  and  $C_{PA}^0$  denote the concentration of azide at time  $t$  and the initial concentration of azide, respectively. The best fit for the data was obtained with this equation. Greater differences were found in the rate constants calculated from the integrated first order rate equation or from the integrated second order single component equation.<sup>70</sup>

Run 1. A standard solution (10 ml.) was prepared by weighing 0.9864 g. (0.01045 mole) of norbornylene, 0.2616 g. (0.00335 mole) of benzene,

2.1211 g. (0.01183 mole) of diethyl phosphorazidate into a 10-ml. volumetric flask and diluting to volume with carbon tetrachloride at room temperature (23-25°). A 1-ml. sample of this solution was pipetted into an NMR tube and placed in a constant temperature bath at  $45.3 \pm 0.1^\circ$ . The sample was removed at intervals from the bath and cooled to room temperature in a water bath and scanned with the NMR over the region of the benzene, norbornylene and triazoline absorptions. The integrations of the areas of these absorptions were then recorded and repeated 2 - 3 times. The sample was then returned to the constant temperature bath. The time that the sample was at room temperature (about 30 minutes) was not included in the total time recorded since the reaction is at least an order of magnitude slower at room temperature. The results of this run are given in Table V. The concentration of azide at various times was calculated from the measured norbornylene concentration by assuming that the change in azide concentration and the change in norbornylene concentration were the same, i.e. the law of mass action held.

Run 2. A 10-ml. volumetric flask was charged with about 0.5 ml. of azide and about 0.7 ml. of norbornylene. Benzene (0.3323 g., 0.004250 mole) was weighed into the flask and the mixture was diluted to volume with carbon tetrachloride. The initial concentrations of azide and norbornylene were determined by NMR by comparing these integrated areas with that for the known concentration of benzene. Concentrations were: azide, 1.415 m/l.; norbornylene, 1.710 m/l. A small sample (about 1 ml.) of the solution was then pipetted into an NMR tube and placed in a constant temperature bath at  $50.1 \pm 0.1^\circ$ . Analyses and calculations as per Run 1 are shown in Table VI.

TABLE V

THE RATE OF FORMATION OF TRIAZOLINE III AT 45.3°

BY NMR METHOD. RUN 1

TIME (min.)	C <sub>PA</sub> (m./l.)	C <sub>NB</sub> (m./l.)	10 <sup>4</sup> k (liters/ mole-min.)
00	1.183	1.045	----
720	1.057	0.919	1.82
960	0.933	0.795	2.57
1140	0.846	0.708	3.82
1320	0.753	0.615	4.24
1470	0.794	0.656	3.38
2190	0.793	0.655	2.38
2500	0.702	0.564	2.70

k (average) =  $3.28 \times 10^{-4}$  l./mole-min.



TABLE VI  
THE RATE OF FORMATION OF TRIAZOLINE III AT 50.1°  
BY NMR METHOD. RUN 2

TIME (min.)	C <sub>PA</sub> (m./l.)	C <sub>NB</sub> (m./l.)	10 <sup>4</sup> k (liters/ mole-min.)
00	1.415	1.710	-----
660	0.862	1.214	7.86
780	0.756	1.051	6.04
915	0.649	0.944	6.86
1076	0.724	1.019	4.82
1423	0.679	0.974	4.09
1574	0.448	0.743	5.07
1650	0.361	0.656	8.38

k (average) =  $6.16 \times 10^{-4}$  l./mole-min.

Run 3. A 10-ml. volumetric flask was charged with norbornylene and azide. Benzene (0.3327 g., 0.00426 mole) was added and the mixture diluted to volume with carbon tetrachloride. The initial concentrations determined by NMR as per run 2 were found to be; azide, 1.051 m/l.; norbornylene, 2.760 m/l. A 1-ml. sample was pipetted into an NMR tube and thermostated at  $55.8 \pm 0.1^{\circ}$ . Analyses and calculations as in Run 1 are shown in Table VII.

Run 4. A 10-ml. volumetric flask was charged with norbornylene and azide and 0.3480 g. (0.00446 mole) of benzene was added. The mixture was diluted to volume with carbon tetrachloride. The initial concentrations determined by NMR as per runs 2 and 3 were found to be; azide, 1.303 m/l.; norbornylene, 2.260 m/l. A 1-ml. sample was pipetted into an NMR tube and thermostated at  $60.0 \pm 0.1^{\circ}$ . Analyses and calculations as in run 1 are shown in Table VIII.

Analysis of Norbornylene Solutions by NMR. Several standard solutions containing norbornylene and benzene in carbon tetrachloride were prepared and analyzed for norbornylene concentration by comparison with the internal standard, benzene, to check the NMR method for accuracy in determining the norbornylene concentration. The results are shown in Table IX.

Differential Thermal Analysis Apparatus. A photograph and a schematic drawing of the apparatus used to study the decomposition of triazoline are shown in Plate XXI and Figure 5, respectively. The apparatus shown consisted of a copper sample block heated in a sand bath by a Variac-controlled heating mantle, sample and reference cells, a chromel-alumel differential thermocouple (DTC), a d.c. amplifier, and a strip chart recorder.

TABLE VII

THE RATE OF FORMATION OF TRIAZOLINE III AT 55.8°

BY NMR METHOD. RUN 3

TIME (min.)	C <sub>PA</sub> (m./l.)	C <sub>NB</sub> (m./l.)	10 <sup>3</sup> k (liters/ mole-min.)
00	1.051	2.760	-----
620	0.314	2.023	1.34
827	0.201	1.910	1.45
1067	0.251	1.960	0.95
1365	0.086	1.794	1.41

k (average) =  $1.40 \times 10^{-3}$  l./mole-min.

TABLE VIII

THE RATE OF FORMATION OF TRIAZOLINE III AT 60.0°

BY NMR METHOD. RUN 4

TIME (min.)	C <sub>PA</sub> (m./l.)	C <sub>NB</sub> (m./l.)	10 <sup>3</sup> k (liters/ mole-min.)
00	1.360	2.26	-----
303	0.860	1.755	8.43
407	0.700	1.600	9.44
520	0.710	1.610	7.15
649	0.540	1.440	8.79
1350	0.223	1.190	7.06

k (average) =  $8.35 \times 10^{-3}$  l./mole-min.

TABLE IX  
ANALYSES OF NORBORNYLENE SOLUTIONS  
BY NMR

SAMPLE NO.	NORBORNY- LENE (g.)	NORBORNY- LENE (mole)	BENZENE (mole)	NORBORNYLENE (mole) found by NMR
1	1.6131	0.01715	0.0103	0.01728
2	1.2572	0.0134	0.00406	0.01299
3	1.3400	0.0142	0.00480	0.01385

$$\% \text{ of theory} = \frac{\text{norborylene by NMR}}{\text{norborylene weighed}} = 98.03$$

Several types of sample and reference cells were constructed, most of which were found unsatisfactory. Stirred cells made of 3/4-in. by 4-in. pyrex test tubes, heated in an oil bath, similar to those described by Borschardt and Daniels were tried. This arrangement was found unsatisfactory because it was difficult to maintain an even temperature throughout the system. Very small temperature gradients were sensed by the DTC and caused an erratic base line. Slightly smaller cells in which more rapid stirring was possible were no more successful even when light mineral oil or water was used in the heating bath. The best arrangement that gave a steady base line over the temperature range studied consisted of using small (0.275-in.) round-bottom thin-walled glass cells placed in a 1-in. copper block heated by means of a heating mantle. The copper block (1.0-in. diameter by 2-in. cylinder) was drilled to accommodate the 2 sample cells and an iron-constant thermocouple to measure the temperature of the block. There was no discernible baseline drift when a scan of the temperature range (25-160<sup>0</sup>) was made with the sample and reference cells filled with diglyme or silica gel.

The most satisfactory DTC found was chromel-alumel made of 0.012-in. thermocouple wire. Copper-constantan and iron-constantan DTC's were tried but it was difficult to get reproducible results, probably because of the difficulties in forming a small uniform bead. A uniform bead appears to be a necessity, for when thermocouples with non-uniform beads were used a great deal of baseline drift was observed. An attempt to measure the sample temperature by fusing 2 thermocouples together in the sample and measuring the sample temperature with a potentiometer or a recorder also gave baseline drift. This was apparently due to the fact

that heat loss through the thermocouple leads of the sample cell was greater than the heat loss from the reference cell. The thermocouples were centered in the sample and reference cells in soft glass capillaries held in place with a vented 1-hole cork stopper.

No difficulties were encountered with the high gain d.c. amplifier (Leeds and Northrup d.c. null detector 9834-2). This amplifier was found to be essentially noise-free and linear in its response with gains up to 20,000 (see procedure below).

The inexpensive Heathkit strip chart recorder that was used to record the amplified output of the DTC was trouble-free throughout the study. Slower chart drive motors which would be useful to eliminate the need to transfer data to measure areas and thus increase the versatility of the instrument, are recommended.

The Leeds and Northrup temperature potentiometer (temperature corrected for an iron-constantan thermocouple) was checked repeatedly with a Minneapolis-Honeywell (Rubicon) potentiometer and found to be operating satisfactorily.

The Rate of Decomposition of Triazoline III by DTA. Tables X, XI, and XII summarize data from three of the many runs that were made in this study. Tables X and XI are typical data obtained when diglyme (the reaction solvent) was used as reference. Table X shows data from a run using silica gel as reference material. A typical run is as follows: (Table XI) 0.1094 g. (0.0004 mole) of triazoline and 0.2885 g. of diglyme were charged to the DTA cell and placed in one hole in the block. A reference cell containing an equivalent amount of silica gel was placed in the other hole in the block. The DTC was carefully centered in the sample

TABLE X

THE RATE OF TRIAZOLINE III DECOMPOSITION BY DTA<sup>a</sup>. RUN 2

Temperature (°K.)	$\Delta T$ (mm.)	a (Sq. mm.)	A-a (Sq. mm.)	$10^3 \Delta T / (A-a)$ (mm. <sup>-1</sup> .)
368	11	45	14857	0.742
372	20	191	13905	1.44
376	36	364	13732	2.63
380	58	805	13291	4.36
384	86	1518	12478	6.88
388	118	2472	11624	10.18
392	148	3798	10298	14.38
396	178	5312	8784	20.3
400	200	7203	6893	29.1
404	208	9252	4854	42.8
408	183	11303	2794	65.2
412	143	12926	1170	122.0
416	94	13075	1021	92.10
420	47	13781	315	149.0

a. The total area under the curve (A) was 14096 mm.<sup>2</sup>. The area under the curve at the various temperatures is A.  $\Delta T / (A-a)$  is the first order rate constant, with units of mm.<sup>-1</sup> in this case according to the simplified rate equation of Borchardt and Daniels (see discussion).<sup>18</sup>



TABLE XI

THE RATE OF TRIAZOLINE III DECOMPOSITION BY DTAA<sup>a</sup>. RUN 3

Temperature (°K.)	$\Delta T$ (mm.)	a (Sq. in.)	A-a (Sq. in.)	$\Delta T/(A-a)$ (mm./Sq. in.)
372.0	5	0.08	17.64	0.283
380.0	22	0.40	17.32	1.270
387.4	56	1.61	16.11	3.476
394.7	94	3.91	12.20	7.705
401.8	126	7.31	10.41	12.104
408.6	135	11.46	6.26	21.645
415.1	98	15.31	2.41	82.158
421.6	32	17.40	0.32	100.00

a. Total area under curve (A) was 17.72 in.<sup>2</sup>.  $\Delta T$  in mm. can be converted to °K. by multiplying by 0.0594°/mm.

TABLE XII

THE RATE OF TRIAZOLINE III DECOMPOSITION BY DTA<sup>a</sup>. RUN 35

Temperature (°K.)	$\Delta T$ (in.)	a (sq. cm.)	A-a (sq. cm.)	$10^3 \Delta T / (A-a) (\text{cm}^{-1})$	$10^{-1} k (\text{min.}^{-1})^b$
376.2	0.10	0.4	106.7	0.109	.0529
380.1	0.20	1.2	105.9	0.218	0.1057
383.7	0.38	2.5	104.6	0.409	0.1984
387.2	0.58	5.4	101.7	0.651	0.3186
390.6	0.76	9.4	97.7	0.900	0.4365
394.2	1.00	14.6	92.5	1.25	0.6063
297.7	1.26	20.1	87.0	1.68	0.8148
401.1	1.60	29.2	77.9	2.38	1.1543
404.2	2.00	39.3	67.8	3.42	1.6587
407.4	2.12	49.9	57.2	4.28	2.076
410.8	2.10	61.5	45.6	5.33	2.585
213.7	1.92	75.3	31.8	6.99	3.390
416.4	1.60	86.2	20.8	8.84	4.287
419.7	1.18	94.4	12.7	10.8	5.238
421.8	0.78	99.9	7.2	12.5	6.063
425.6	0.45	103.2	3.9	13.4	6.499

a. Total area under curve (A) was 107.1 cm.<sup>2</sup>.

b. The first order reaction rate constants were obtained in units of min.<sup>-1</sup> by multiplying  $\Delta T / (A-a)$  by 48.5, the appropriate conversion factor determined by calibration of the system described below.

material and reference material and the block was enclosed in a glass cylinder filled with glass wool to insulate and protect the cells and block from air currents. The block was then heated in a sand bath by setting the Variac at 60 volts. The temperature of the block was estimated to  $0.1^{\circ}\text{C}$  at 30-second intervals with the temperature potentiometer. The DTA curve was obtained in about 25 minutes at a heating rate of  $3^{\circ}/\text{min.}$  with an amplifier sensitivity setting of 3.0. Figure 6 is the curve obtained after the original tracing had been transferred to a smaller scale for convenience in measuring areas. The maximum in the curve occurred at  $134.9^{\circ}$ .

The areas of the DTA curves obtained were measured with a K & E compensating polar planimeter.

DTA Run 2. A small sample (about 0.04 g.) of triazoline in 0.30 ml. of diglyme was charged to the sample cell. Diglyme (0.30 ml.) was charged to the reference cell and the cells were placed in the block with the DTC centered properly. A heating rate of about  $4.0^{\circ}/\text{min.}$  was obtained by setting the Variac at 65 volts. The amplifier sensitivity was set at 3.0 and the recorder range was 0-250 mv. The temperatures given in Table X are at 1-min. intervals. The areas were measured by counting the squares on the graph paper to which the original tracing had been transferred. The factor for converting the vertical axis ( $\Delta T$ ) from mm. to  $^{\circ}\text{K}$  was not calculated for this run.

DTA Run 3. A 2.7316-g. sample of triazoline was weighed into a 10-ml. volumetric flask and diluted to volume with diglyme. This sample (0.30 ml.) and 0.30 ml. of diglyme were pipetted into the sample cell and reference cell respectively, which were placed in the sample block. The

same procedure as for Run 2 was then followed except the amplifier sensitivity setting was 3.50. Areas were measured in square inches with a planimeter.

Calibration of the DTA System. The amplifier and recorder were calibrated so that  $\Delta T$  could be determined in degrees by multiplying the change in potential measured in millivolts with the recorder by the appropriate amplification factor. The procedure is as follows: a known potential was placed across the input lead of the amplifier with the Minneapolis Honeywell potentiometer and the amplifier output was measured with the recorder. Table XIII is a summary of the amplification obtained at various settings. The system was calibrated before each run when the rate constants were calculated in  $\text{min.}^{-1}$ . Calculation of the factor is as follows:

$$\text{amplification factor} \left[ \frac{\text{mv. input}}{\text{mv. output}} \right] \times \frac{^{\circ}\text{C}}{\text{mv.}} \quad (\text{i.e. } 1/\text{thermocouple output per degree})$$

$$= \text{ } ^{\circ}\text{C}/\text{mv. measured on the chart paper}$$

Kinetics of the Reaction of N,N-Dimethylaniline and Ethyl Iodide by DTA. The kinetics of the reaction of N,N-dimethylaniline and ethyl iodide were determined in order to check the use of small cells. The ratio of reactants used was the same as that of Borchardt and Daniels.<sup>30</sup> Small cells described above rather than the large stirred cells used by Borchardt and Daniels were used. A solution of 17.5 ml. of N,N-dimethylaniline and 2.5 ml. of ethyl iodide was prepared. Immediately after mixing the reactants, 0.30 ml. of the solution was pipetted into the sample cell. The sample cell and reference cell containing 0.30 ml. of N,N-

TABLE XIII

## CALIBRATION OF THE DTA SYSTEM

Sensitivity Setting	Input, Microvolts	Output, Millivolts
3.0	5.0	28.0
	10.0	58.8
	20.0	88.7
4.0	5.0	46.3
	10.0	141.1
	15.0	212.0
5.0	2.0	73.7
	3.0	112.5
	4.0	137.4

dimethylaniline were placed in the block with the DTC properly centered. A setting of 4.0 on the sensitivity of the amplifier with the recorder range set at 0-100 mv. was used. The DTA curve for the reaction was obtained in 34 minutes. Temperature range for the reaction was 75° to 165° with the maximum occurring at 131°. Data from this run are shown graphically in Figure 7. Borchardt and Daniels<sup>18</sup> data by DTA and Moelwyn-Hughes<sup>50</sup> data by conventional methods are included for comparison.

The Enthalpy of Triazoline III Decomposition Determined by DTA. The enthalpy change for the decomposition of triazoline to form products was determined by comparing the area of the DTA curve (Table V) with the area of the DTA curve obtained from the fusion of o-toluic acid for which the enthalpy change is reported<sup>15</sup> to be 35.4 cal./gram. A 0.1527-g. sample of o-toluic acid was weighed into the sample cell. Approximately the same weight of silica gel was used as reference material. The DTA curve obtained as described above for the decomposition had an area of 31.88 sq. in. The DTA curve obtained under identical conditions for the decomposition of 0.1094 g. (0.0004 mole) of triazoline III had an area of 37.00 sq. in. (measured on the chart paper before being transferred to a smaller scale). This corresponds to an enthalpy change of -15.7 kcal./mole, calculated as follows. (The enthalpy change is negative because the observed pen deflection for the fusion of o-toluic acid, an endothermic reaction, was in the opposite direction as that for the decomposition of triazoline).

$$\frac{0.1527 \text{ (g. toluic acid)} \times 35.4 \text{ cal./g.}}{31.88 \text{ sq. in. (toluic acid DTA)}} \times \frac{37.00 \text{ sq. in. (triazoline III dec.)}}{0.0004 \text{ mole of triazoline III}} = -15.7 \text{ kcal./mole}$$

Apparatus for Measurement of the Rate of Nitrogen Evolution During the Decomposition of Triazoline III. The apparatus used to study the rate of decomposition of triazoline is shown in Plate XX and schematically in Figure 2. It consisted of a 500-ml. glass bulb fitted with a vacuum stopcock at the top to which a mechanical vacuum pump was attached, a thermometer (0.05° divisions) to measure temperature of the gas during a run, a vacuum stopcock at the bottom to allow nitrogen produced during a run to escape into the evacuated bulb, and a side arm attached by means of a 5/5 mm. standard ball joint to a mercury manometer (780 mm.) to measure the pressure of nitrogen in the bulb. By means of a glass capillary T (0.5 mm.) attached to the bottom stopcock of the bulb a second mercury manometer was attached (to measure the pressure of nitrogen in the reaction flask itself). The manometer was connected to the T-joint by means of a 5/5 mm. capillary ball-joint, and the reaction flask (50-ml. capacity) was connected by means of capillary rubber tubing from a tight fitting rubber stopper to the condenser of the reaction flask, which was fitted with a 14-mm. standard tapered joint. This apparatus was then placed over a 10-gallon-capacity, thermostated oil bath in such a manner that the reaction flask could be raised and lowered into the bath conveniently. This arrangement proved quite satisfactory since the glass bulb, even though it was directly over the bath, was high enough that temperature changes in it were very small even with the bath temperature greater than 110°C.

The volume of the bulb was determined by weighing the bulb (empty and filled) to the top of the side arm with distilled water. The volume at 24.5° was found to be 504.6 ml.. A conversion factor used with the system at 24.5° to convert from pressure in mm. to moles of nitrogen was

calculated with the ideal gas law to be  $2.712 \times 10^{-5}$  moles/mm. The average temperature of the gas in the bulb, which varied less than  $0.5^{\circ}$  during a run, was used to calculate the appropriate conversion factor for that particular run.

Calibration of the system was accomplished by injecting a known amount of nitrogen into the reaction flask, adjusting the pressure on the reaction flask to 0.0 mm. by allowing the gas to escape into the bulb through the bottom stopcock which had been evacuated to less than 0.1 mm. absolute, and observing the pressure change in the bulb. Figure 11 shows the linear relationship that was obtained.

Procedure for Measurement of Rate of Nitrogen Evolution During the Decomposition of Triazoline III. An identical procedure was used in all runs for which the data are given in the following tables. A general procedure is therefore outlined here. Solvent (10 to 25 ml.) was added to the reaction flask and allowed to equilibrate in the thermostated bath for about 15 minutes. Since the reaction is consecutive first order (see Results and Discussion), the amount of solvent used was measured with a graduated cylinder. During the equilibration time, the entire system was flushed 3 - 5 times with nitrogen. This was accomplished by evacuating the bulb to less than 0.1 mm. and then allowing dry, lamp-grade nitrogen to fill the system through the reaction flask to a pressure of about 50 mm. gauge. Triazoline III (1 - 3 g.) was then quickly added to the system which was then sealed. The pressure on the system was maintained at 0.0 mm. gauge by allowing the nitrogen produced to escape through the bottom stopcock into the evacuated bulb. The pressure of nitrogen (i.e. amount of nitrogen given off) was measured at time  $t$  by closing the bottom



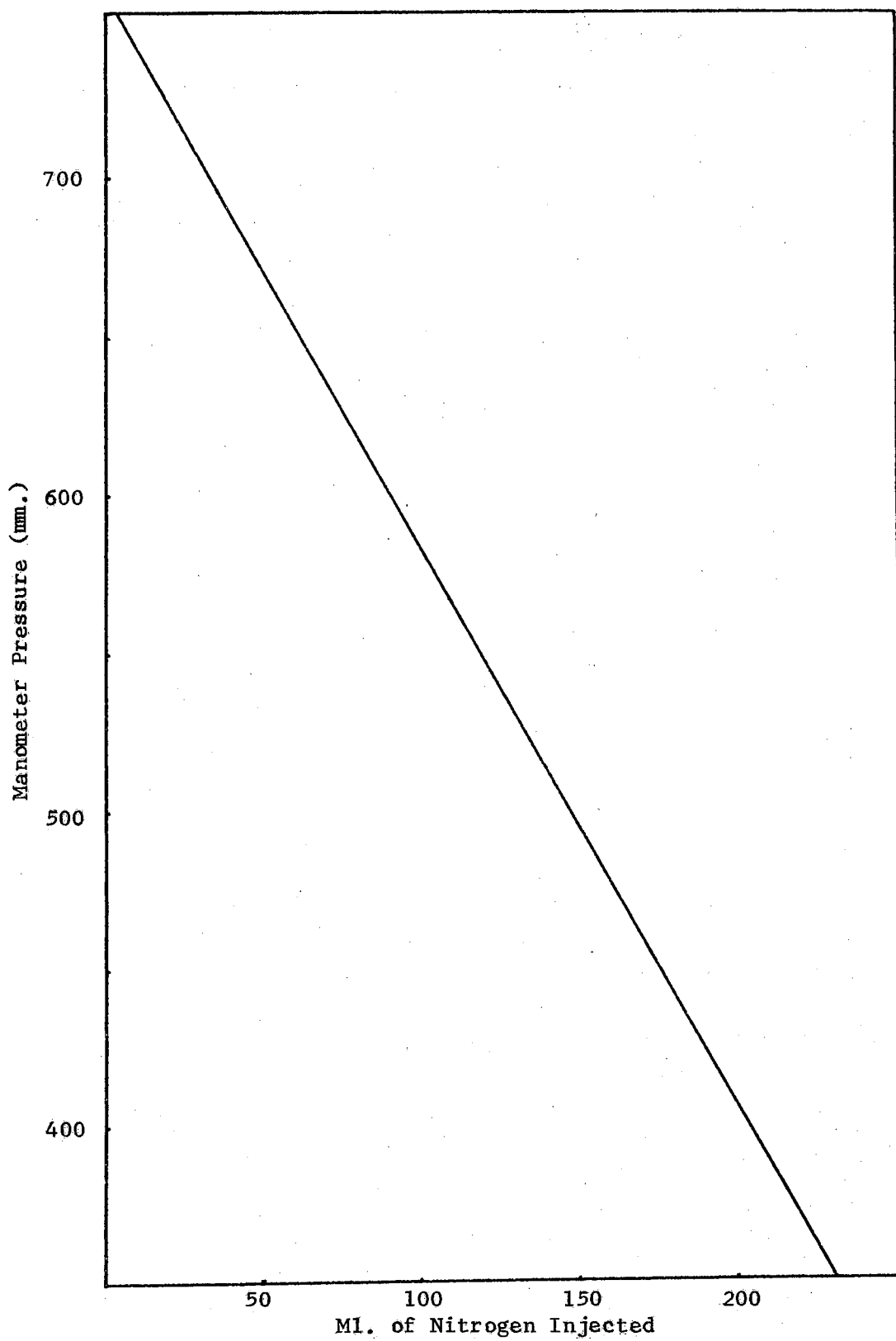


Figure 11. Calibration of Nitrogen Evolution Apparatus.

stopcock at time  $t$  and observing the pressure in the bulb. The release of nitrogen was initiated again to maintain zero pressure on the reaction system until the next reading was made. The run was terminated when the extent of reaction reached 0.8 to 0.9. In a few of the runs (these are indicated in the tables), the initial concentration of triazoline III by weight was in doubt due to mechanical losses during the weighing. In these runs the reaction was allowed to go nearly to completion and the final volume of nitrogen was used to calculate the initial concentration.

The solvents used in this study were reagent grade. They were dried over type 5-A molecular sieve for at least 48 hours before use. Preparation of the triazoline used is described elsewhere.

Partial pressure of the solvent during the run was not corrected for since it was found that when solvent alone was sealed in the reaction flask and the pressure on the system adjusted 10 to 20 times a negligible ( $<0.5$ -mm. pressure change) was observed.

Tables XIV to XX show the data measured and calculated in this study.

Calculation of Activation Energy and Entropy of Activation for the Decomposition of Triazoline III. Activation energies for the formation of the dipolar intermediate IV and the decomposition of IV were calculated from the slope of the Arrhenius plot of the data for the rate constants  $k_a$  and  $k_b$ , respectively. Figure 3 is the Arrhenius plot for the  $k_a$  and Figure 4 is the Arrhenius plot for the  $k_b$ . The entropy of activation  $\Delta S^*$  was calculated from transition state theory. Table III shows these data and the average values of  $k_a$  and  $k_b$  at various temperatures.

Calculation of the Rate Constants for the Decomposition of Triazoline III. The following computer program in Fortran IV was used to

TABLE XIV<sup>a</sup>

DECOMPOSITION OF TRIAZOLINE III AT 371.2°K.

Time (min.)	Nitrogen Evolved X 10 <sup>3</sup> (moles) <sup>b</sup>	10 <sup>2</sup> k <sub>a</sub> (min. <sup>-1</sup> )	10 k <sub>b</sub> (1) (min. <sup>-1</sup> )	10 k <sub>b</sub> (2) (min. <sup>-1</sup> )
35.00	.4352	.5324	.7151	.7430
45.00	.6256	.4800	.9694	.9694
55.00	.7888	.4584	1.201	1.201
66.00	.9520	.5901	.4931	.4992
75.00	1.115	.5129	.7813	.7813
85.00	1.264	.4902	1.032	1.032
95.00	1.400	.5686	.4910	.4910
105.00	1.550	.5465	.5747	.5747
115.00	1.684	.5781	.4538	.4538
125.00	1.822	.5753	.4628	.4628
175.00	2.393	.4819	-1.544	.0000
180.00	2.434	0000	0000	.0000

a The initial concentration of triazoline III was  $4.107 \times 10^{-3}$  moles.  
Solvent was diglyme.

b The nitrogen evolved was calculated by multiplying the pressure in the  
bulb by the conversion factor  $2.720 \times 10^5$  moles/mm.

TABLE XV<sup>a</sup>

## DECOMPOSITION OF TRIAZOLINE III AT 381.3°K

Time (min.)	Nitrogen Evolved 10 <sup>3</sup> (moles) <sup>b</sup>	10 k <sub>a</sub> (min. <sup>-1</sup> )	k <sub>b</sub> (1) (min. <sup>-1</sup> )	k <sub>b</sub> (2) (min. <sup>-1</sup> )
15.00	1.114	.1286	.2086	.2086
20.00	1.617	.1375	.1760	.1760
25.00	2.120	.1270	.2364	.2364
30.00	2.554	.1356	.1741	.1741
35.00	2.989	.1267	.2603	.2603
40.00	3.370	.1253	.2890	.2890
45.00	3.723	.1231	.3648	.3648
50.00	4.049	.1199	.6580	.6580
55.00	4.348	.1156	-2.2278	.0453
60.00	4.620	.2258	.0323	.0341
65.00	4.865	.1165	3.3747	3.3747
70.00	5.109	.1238	.2355	.2355
75.00	5.354	.0966	-0.0597	.0000
125.00	6.822	.3949	.0090	.0134
140.00	7.066	.1014	-.2114	.0000
155.00	7.365	.0000	.0000	.0000

a The initial concentration of triazoline III was  $9.185 \times 10^{-3}$  moles. Solvent was diglyme.

b The nitrogen evolved was calculated by multiplying the pressure in the bulb by the conversion factor  $2.718 \times 10^{-5}$  moles/mm.

TABLE XVI<sup>a</sup>

## DECOMPOSITION OF TRIAZOLINE III AT 391.2°K

Time (min.)	Nitrogen Evolved 10 <sup>3</sup> (moles) <sup>b</sup>	10 k <sub>a</sub> (min. <sup>-1</sup> )	k <sub>b</sub> (1) (min. <sup>-1</sup> )	k <sub>b</sub> (2) (min. <sup>-1</sup> )
5.00	.1087	.3680	.1831	.2411
10.00	.6387	.4001	.2097	.2365
15.00	1.114	.3900	.2519	.2534
20.00	1.494	.4080	.2219	.2219
25.00	1.821	.4075	.2230	.2230
31.00	2.133	.4981	.1237	.1271
35.00	2.337	.4981	.1270	.1300
40.00	2.541	.5131	.1195	.1225
45.00	2.704	.6590	.0760	.0817
50.25	2.867	.7812	.06688	.0735
55.00	2.989	1.024	.09509	.1718
61.75	3.125	.1238	.2355	.0000

a The initial concentration of triazoline III was  $3.262 \times 10^{-3}$  moles. Solvent was diglyme.

b The nitrogen evolved was calculated by multiplying the pressure in the bulb by the conversion factor  $2.718 \times 10^{-5}$  moles/mm.

TABLE XVII<sup>a</sup>

## DECOMPOSITION OF TRIAZOLINE III AT 399.7°K

Time (min.)	Nitrogen Evolved 10 <sup>3</sup> (moles) <sup>b</sup>	10 k <sub>a</sub> (min. <sup>-1</sup> )	k <sub>b</sub> (1) (min. <sup>-1</sup> )	k <sub>b</sub> (2) (min. <sup>-1</sup> )
5.00	.3259	.9668	.1863	.2982
10.00	1.222	.8282	.4293	.4293
15.00	1.711	.9257	.3020	.3058
20.00	2.064	.8995	.3391	.3391
25.00	2.281	.6680	-.2151	.2230
30.00	2.390	1.520	.0936	.1821
35.00	2.485	.9548	.2017	.2017
40.00	2.553	1.646	.2565	.5809
45.75	2.620	.4096	-.0048	.0817
55.00	2.634	.7812	.06688	.0000

a The initial concentration of triazoline III was  $2.664 \times 10^{-3}$  moles. Solvent was diglyme.

b The nitrogen evolved was calculated by multiplying the pressure in the bulb by the conversion factor  $2.716 \times 10^{-5}$  moles/mm.

TABLE XVIII<sup>a</sup>

## DECOMPOSITION OF TRIAZOLINE III AT 381.0°K

Time (min.)	Nitrogen Evolved $10^3$ (moles) <sup>b</sup>	$10 k_a$ (min. <sup>-1</sup> )	$k_b$ (1) (min. <sup>-1</sup> )	$k_b$ (2) (min. <sup>-1</sup> )
10.00	.2446	.1075	.2590	.2590
15.00	.4348	.0805	4.3209	4.3209
20.00	.5707	.1536	.0974	.1042
25.00	.8154	.1094	.2971	.2971
30.00	.9784	.0959	-3.4642	.2230
35.00	1.114	.2385	.0335	.0390
40.00	1.304	.1084	.4593	.4593
45.00	1.440	.1181	.1808	.1808
55.00	1.712	.1029	-.6344	.0817
60.00	1.821	.2115	.03034	.0324
65.00	1.929	.1147	.2038	.2038
70.00	2.038	.1238	.2355	.2355

a The initial concentration of triazoline III was  $3.879 \times 10^{-3}$  moles. Solvent was diglyme.

b The nitrogen evolved was calculated by multiplying the pressure in the bulb by the conversion factor  $2.718 \times 10^{-5}$  moles/mm.

TABLE XIX<sup>a</sup>

## DECOMPOSITION OF TRIAZOLINE III AT 381.0°K

Time (min.)	Nitrogen Evolved 10 <sup>3</sup> (moles) <sup>b</sup>	10 <sup>2</sup> k <sub>a</sub> (min. <sup>-1</sup> )	k <sub>b</sub> (1) (min. <sup>-1</sup> )	k <sub>b</sub> (2) (min. <sup>-1</sup> )
20.00	1.253	.6743	-8.922	.2590
25.00	1.539	1.372	.0555	.0607
30.00	1.825	.6460	-.6172	.1042
40.00	2.329	1.259	.0349	.0399
50.00	2.778	.5925	-.1718	.2230
60.00	3.187	1.114	.0304	.0334
70.00	3.527	.6191	-.7430	.4593
80.00	3.908	.8638	-.03668	.0384
100.00	4.535	.4935	-.0383	.0817
115.00	4.916	2.609	.0083	.0096
120.00	5.189	.1757	-.0024	.2038
130.00	5.270	.5003	-.0504	.2355
160.00	5.842	1.844	.0074	.0085
170.00	5.979	.2734	-.0046	.0134
202.00	6.306	.6655	.01881	.0000
240.00	6.850	.2635	.0000	.0000
307.00	7.341	.0000	.0000	.0000

a The initial concentration of triazoline III was  $9.880 \times 10^{-3}$  moles. Solvent was toluene.

b The nitrogen evolved was calculated by multiplying the pressure in the bulb by the conversion factor  $2.725 \times 10^{-5}$  moles/mm.



TABLE XX<sup>a</sup>

## DECOMPOSITION OF TRIAZOLINE III AT 381.3°K

Time (min.)	Nitrogen Evolved 10 <sup>3</sup> (moles) <sup>b</sup>	10 k <sub>a</sub> (min. <sup>a</sup> -1)	k <sub>b</sub> (1) (min. <sup>-1</sup> )	k <sub>b</sub> (2) (min. <sup>-1</sup> )
20.00	3.318	.3078	.2104	.2104
25.00	4.134	.3049	.2175	.2175
30.00	4.828	.2915	.2780	.2780
35.00	5.399	.3062	.2044	.2044
40.00	5.916	.2800	.5031	.5031
45.00	6.324	.2561	-.4996	.0334
50.00	6.650	.4851	.0492	.0528
55.00	6.908	.2013	-.0500	.0000
60.00	7.112	.0493	.0000	.0000

a The initial concentration of triazoline III was  $9.039 \times 10^{-3}$  moles. Solvent was benzonitrile.

b The nitrogen evolved was calculated by multiplying the pressure in the bulb by the conversion factor  $2.720 \times 10^{-5}$  moles/mm.

calculate the rate constants shown in Tables XIV to XX. See Results and Discussion, Chapter II.

```

DIMENSION TITLE(14), AK(20), BK(20,2), C(20), T(20)
2003 FORMAT(4H AO=E16.8, 7H FACT =E16.8, 4H N=15)
1000 FORMAT(13A6, A2)
1001 FORMAT(2E10.5, I2)
1002 FORMAT(2F6.2)
2000 FORMAT(2E20.8)
2001 FORMAT(15, 5X, E12.6)
2002 FORMAT(4H AK=E20.8, 4H BK=E20.8)
3000 FORMAT(1H1, 13A6, A2//)
3002 FORMAT(//7H AKAVE=E20.8)
3001 FORMAT(17H TIME CONC, 12X, 2HAK18X, 3HBK18X, 17X, 3HBK2//(F10.2, 4
1E20.8))
3003 FORMAT(//5H A1=E12.6, 4X, 3HA2=E12.6)

NR=1

NW=3

20 READ(NR, 1000) (TITLE(I), I=1, 14)

READ(NR, 1001) AO, FACT, NPTS

IF (NPTS.EQ.0) GO TO 33

READ(NR, 1002) (T(I), C(I), I=1, NPTS)

WRITE(NW, 3000) (TITLE(I), I=1, 14)

WRITE(NW, 2003) AO, FACT, NPTS

DO 1 I=1, NPTS

1 C(I)=C(I)*FACT

WRITE(NW, 3001) (T(I), C(I), AK(I), BK(I,1), BK(I,2), I=1, NPTS)

A1=C(1)/AO

```

```

NPTSM=NPTS-1

DØ2I=1, NPTSM

A2=C(I+1)/A0

WRITE(NW, 3003)A1, A2

AK(I)=(ALOG((1.-A1)/(1.-A2)))/(T(I+1)-T(I))

N=1

J=1

8 BK(I, N)=AK(I)/((1.-A1)*EXP(AK(I)*T(J))-1.)+AK(I)

WRITE (NW, 2002)AK(I), BK(I, N)

IF(BK(I, N).LT.0.0)GØTØ2

6 CØNI=EXP(-AK(I)*T(J))

WRITE (NW, 2001)J, CØNI

KØUNT=1

4 TEST=CØNI+(AK(I)/(BK(I, N)-AK(I)))*(CØNI-EXP(-BK(I, N)*T(J)))

IF(ABS(TEST-(1.-A1))-0.004(5, 5, 3

3 BK(I, N)=BK(I, N)*TEST/(1.-A1)

WRITE(NW, 2000)TEST, BK(1, N)

KØUNT=KØUNT+1

IF(KØUNT.GT.10)GØTØ5

GØTØ4

5 IF(J.EQ.(I+1))GØTØ2

J=I+1

N=2

A1=A2

GØTØ8

2 CØNTINUE

```

```
NAK=NPTS-1

SUM=0.

DØ1ØI=1,NAK

10 SUM=SUM+AK(I)

ANAK=NAK

AKAVE=SUM/ANAK

WRITE(NW,3001)(T(I),C(I),AK(I),BK(I,1),BK(I,2),I=1,NPTS)

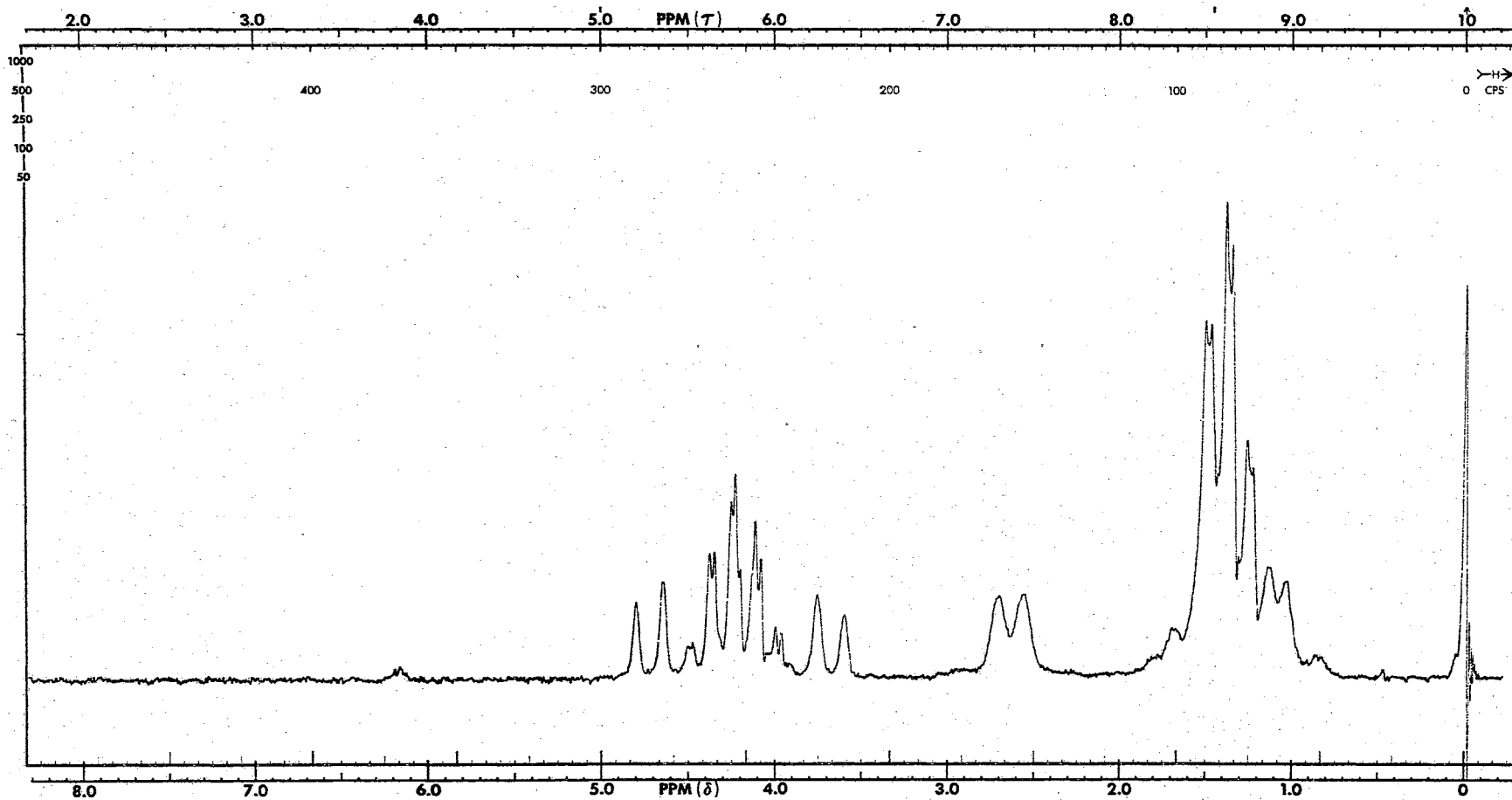
WRITE(NW,3002)AKAVE

GØTØ20

33 CALLEXIT

END
```

Plate I

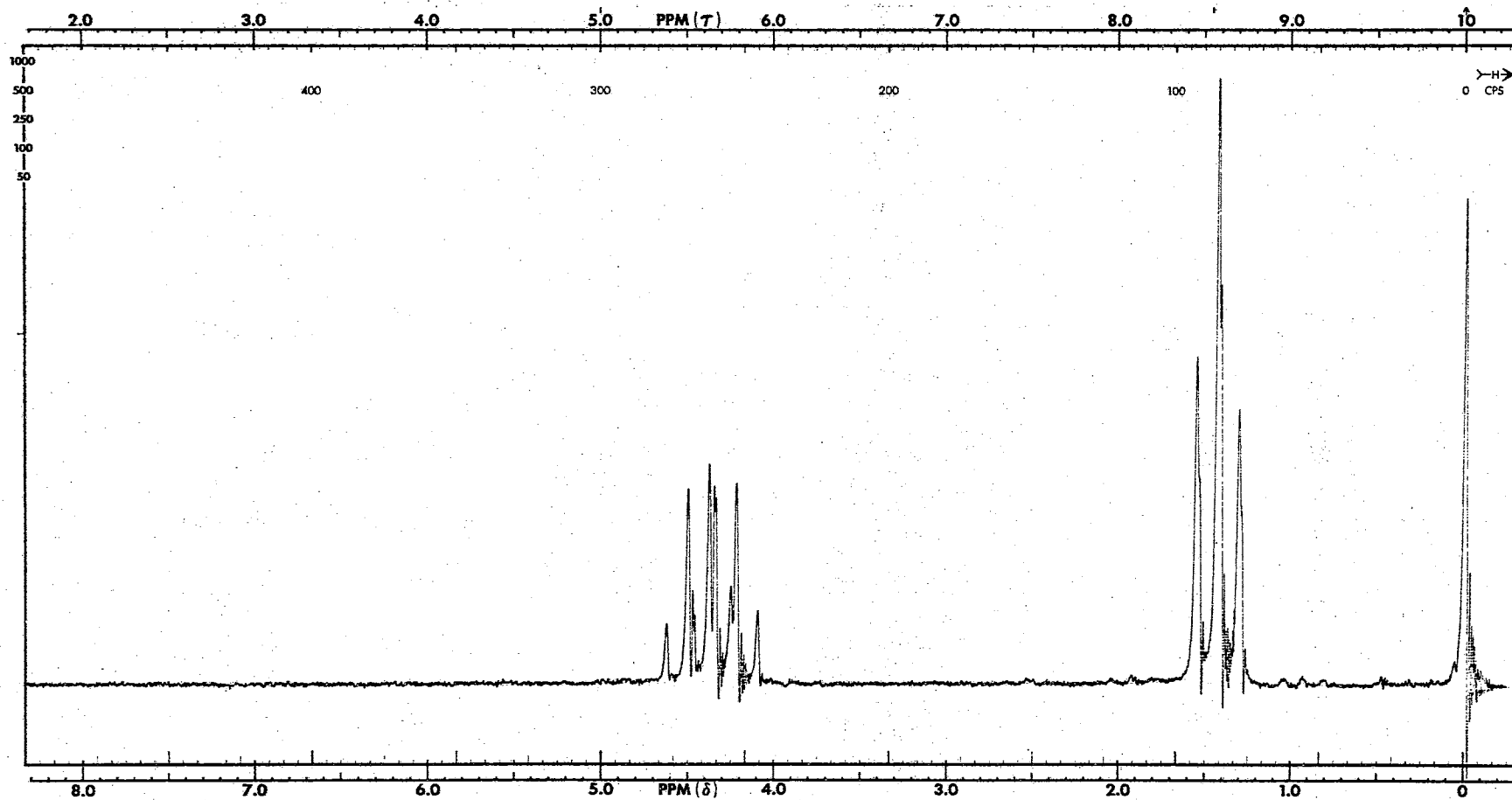


Diethyl (3a,4,5,6,7,7a-hexahydro-4,7-methano-1H-benzotriazol-1-yl)phosphonate (III)

Solvent . . . . . CCl<sub>4</sub>    R.F.Field. . . . . 0.05 mG    S.W. . . . . 500 cps    S.A. . . . . 80

F. B. . . . . 2.0 cps    S.T. . . . . .250 sec    S.O. . . . . .0.0 cps    I.A. . . . . .off

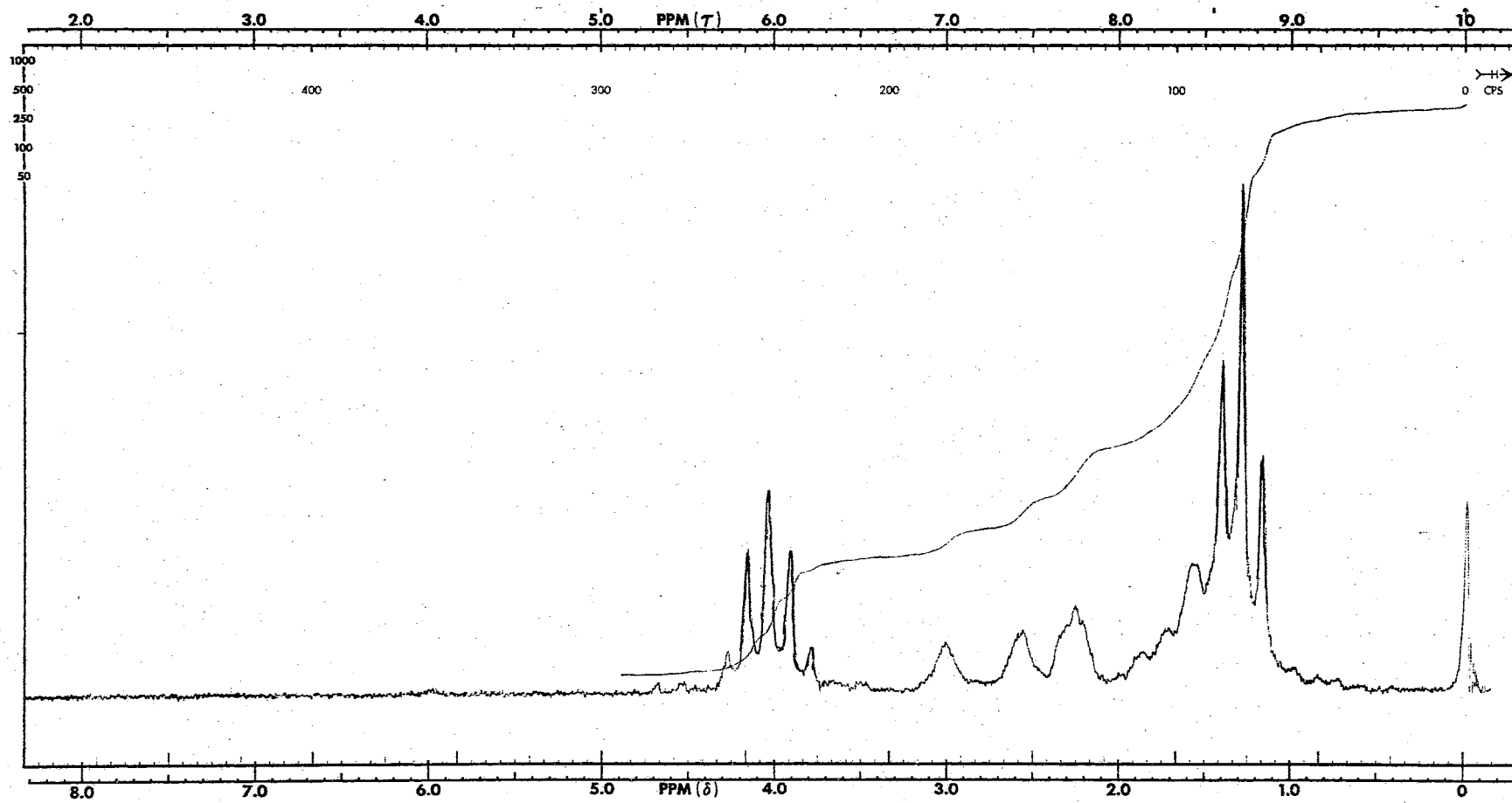
Plate II



Diethyl Phosphorazidate (I)

Solvent. . . . .	.CCl <sub>4</sub>	R.F.Field. . . . .	.0.075 mg	S.W. . . . .	.500 cps	S.A. . . . .	2.5
F. B. . . . .	4.0 cps	S.T. . . . .	.250 sec	S.O. . . . .	.0.0 cps	I.A. . . . .	off

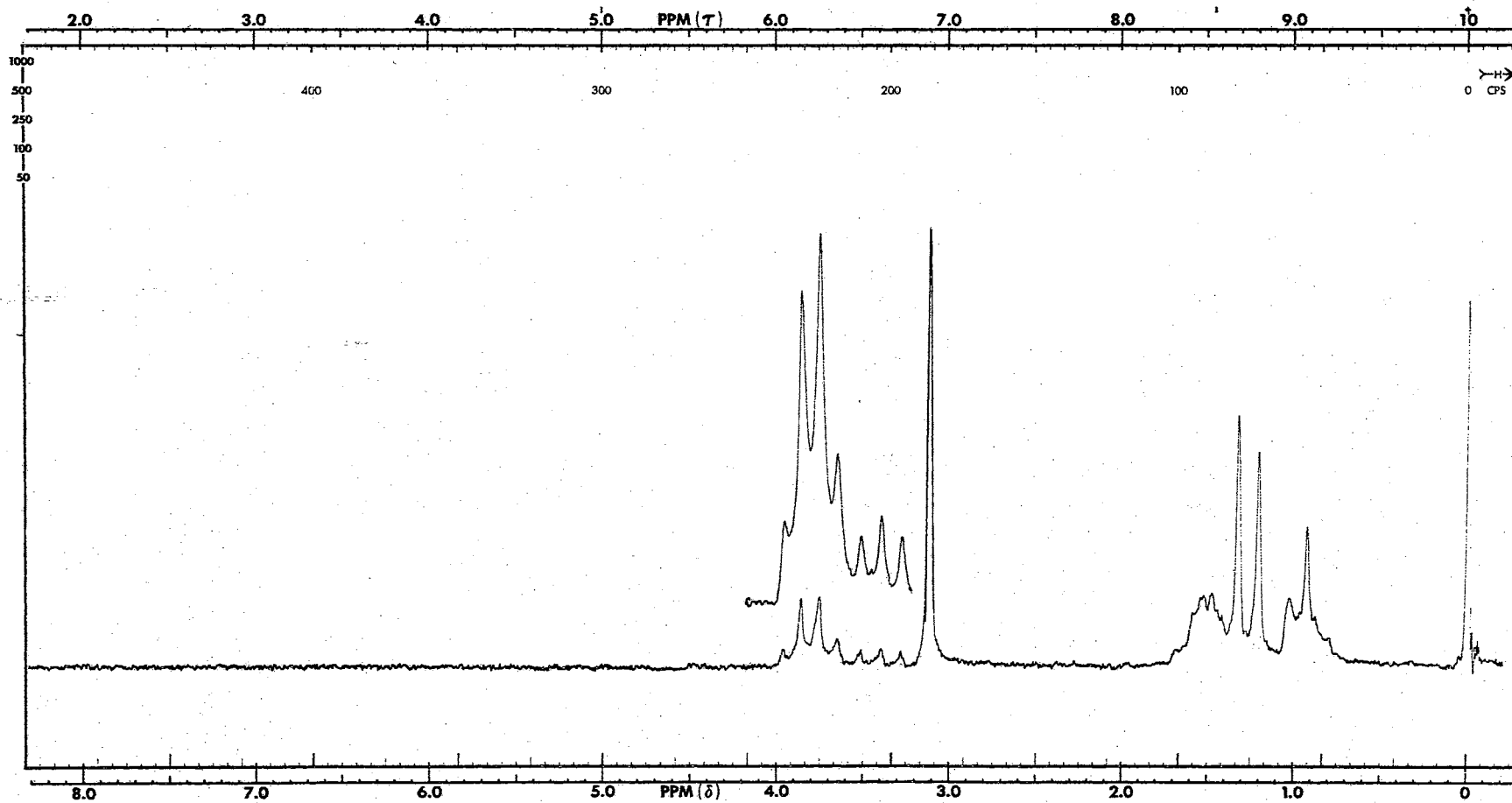
Plate III



Diethyl 2-Norbornylidene phosphoramidate (LXIa)

Solvent. . . . .	.CCl <sub>4</sub>	R.F.Field. . . . .	.0.2 mg	S.W. . . . .	.500 cps	S.A. . . . .	3.2
F.B. . . . .	4.0 cps	S.T. . . . .	.250 sec	S.O. . . . .	.0.0 cps	I.A. . . . .	.16.0

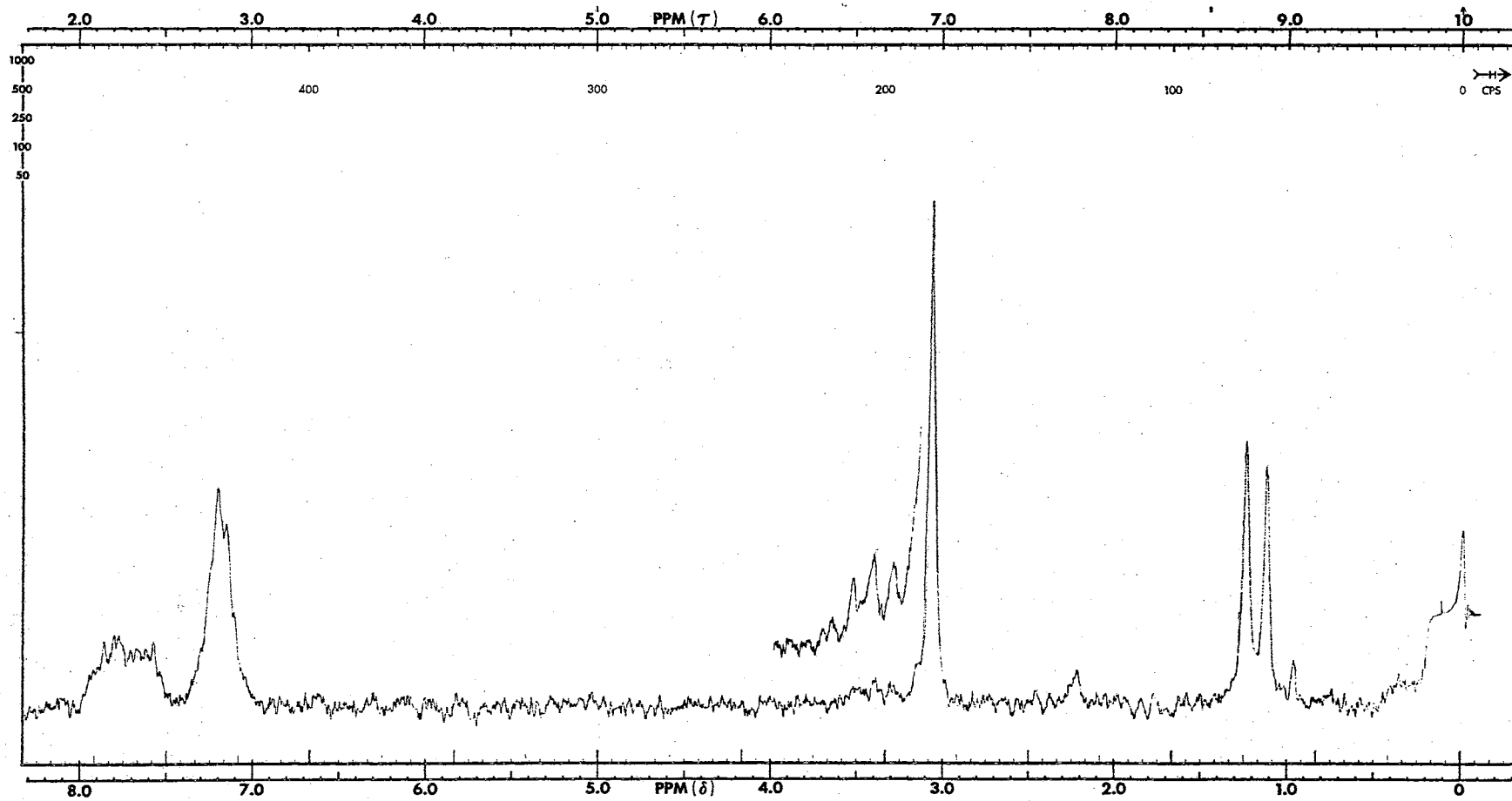
Plate IV



N-(Di-n-butylphosphoryl)-N',N'-dimethylisobutyramidine (LXIc)  
 Solvent. . . . . CCl<sub>4</sub> R.F.Field. . . . . 0.04 mG S.W. . . . . 500 cps S.A. . . . . 20  
 F.B. . . . . 2.0 cps S.T. . . . . 250 sec S.O. . . . . 0.0 cps I.A. . . . . off



Plate V

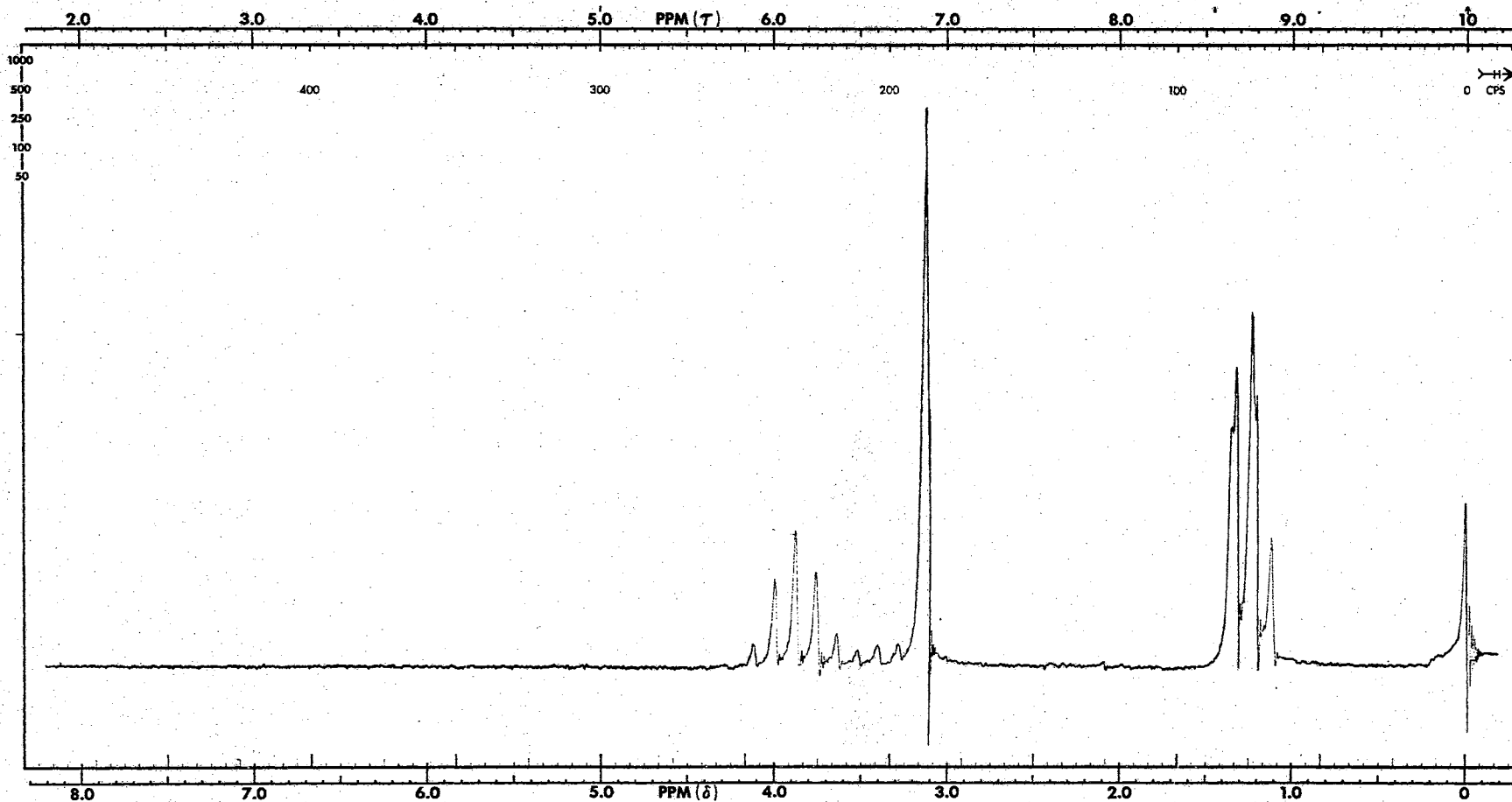


N-(P,P Diphenylphosphinyl)-N',N'-dimethylisobutyramidine (LXIb)

Solvent. . . . . CCl<sub>4</sub>    R.F.Field. . . . . 0.05 mG    S.W. . . . . 500 cps    S.A. . . . . 16.0

F.B. . . . . 0.4 cps    S.T. . . . . 250 sec    S.O. . . . . 0.0 cps    I.A. . . . . off

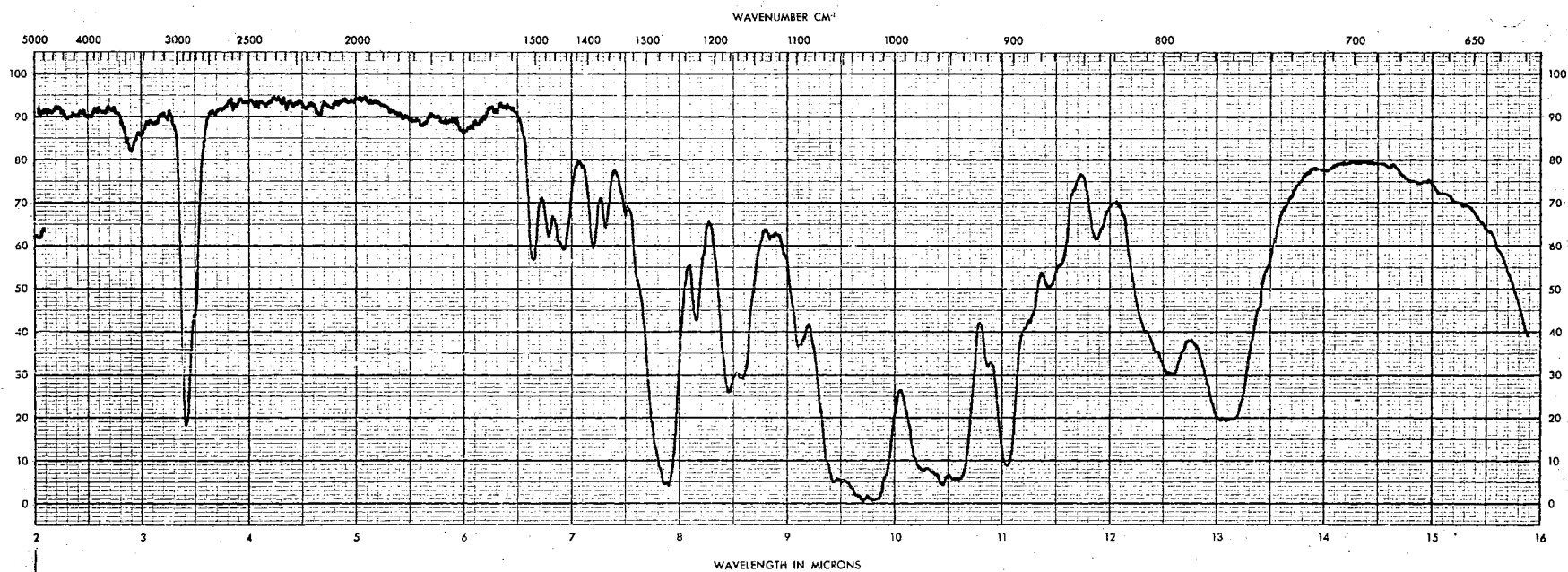
Plate VI



N-(Diethylphosphoryl)-N',N'-dimethylisobutyramidine (LXIa)

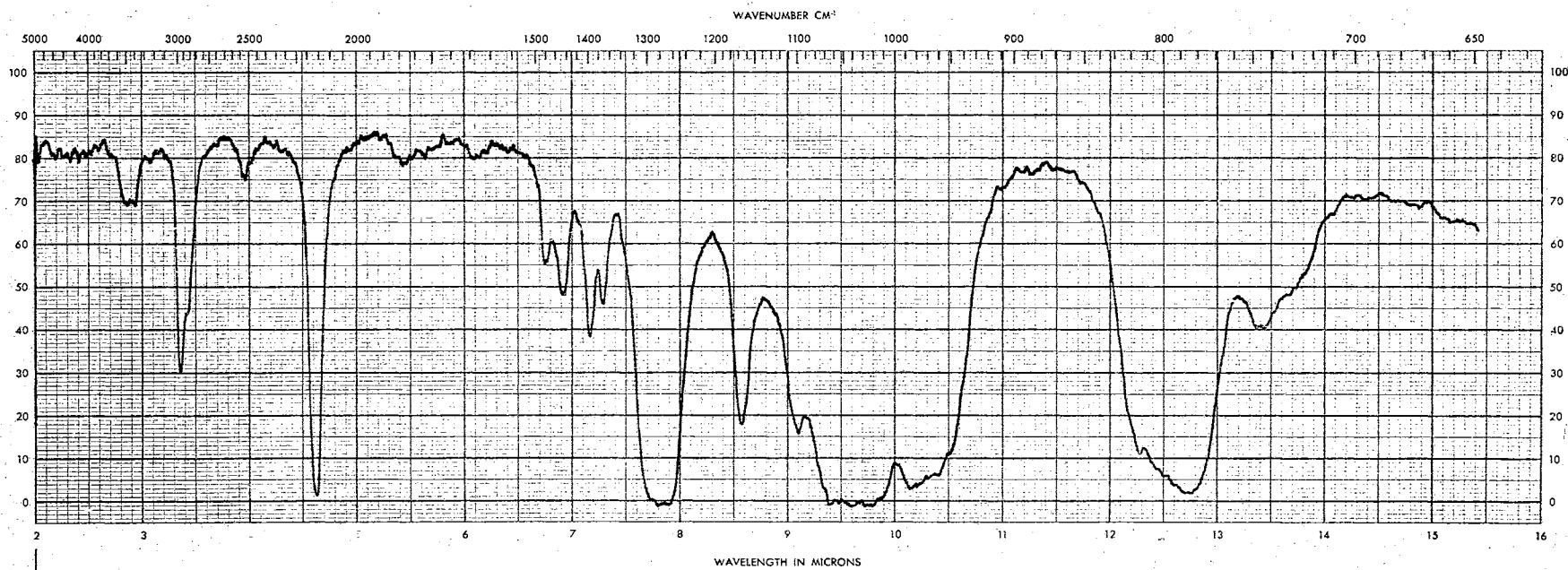
Solvent. . . . .	CCl <sub>4</sub>	R.F.Field. . . . .	0.15 mG	S.W. . . . .	500 cps	S.A. . . . .	4.0
F.B. . . . .	2.0 cps	S.T. . . . .	250 sec	S.O. . . . .	0.0 cps	I.A. . . . .	off

Plate VII



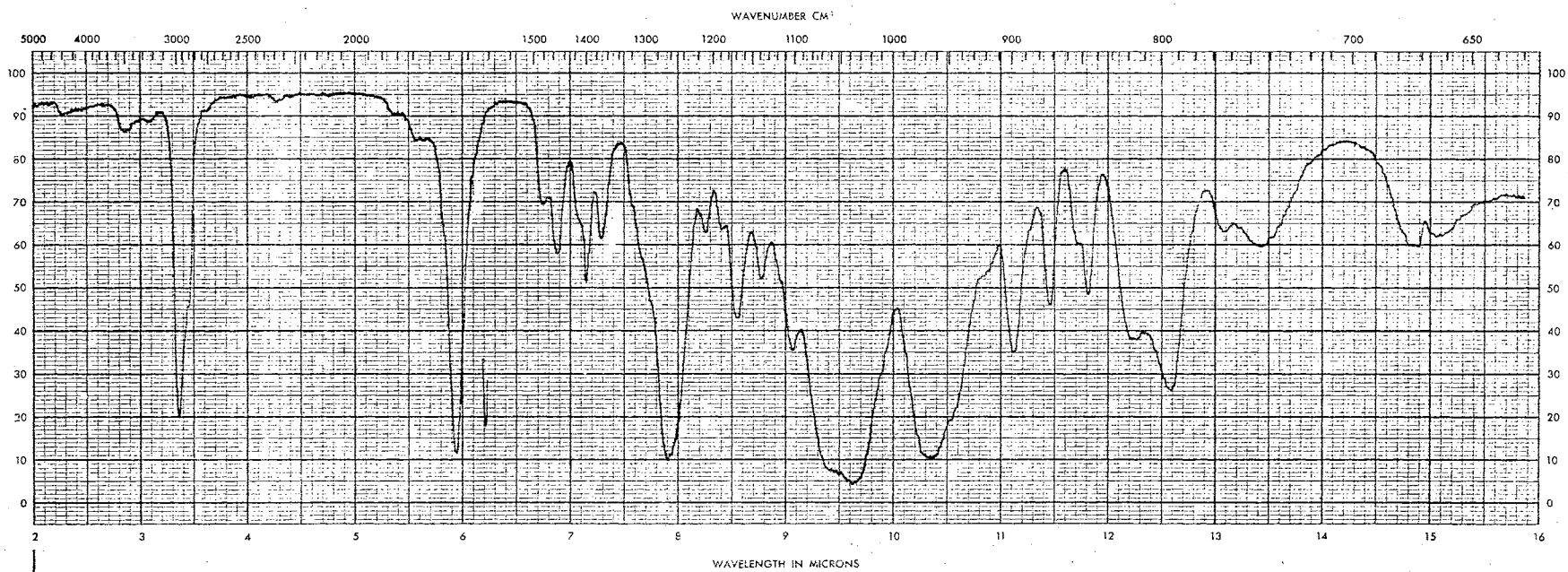
Diethyl (3a,4,5,6,7,7a-hexahydro-4,7-methano-1H-benzotriazol-1-yl) phosphonate (III),  
Film on NaCl Plates

Plate VIII



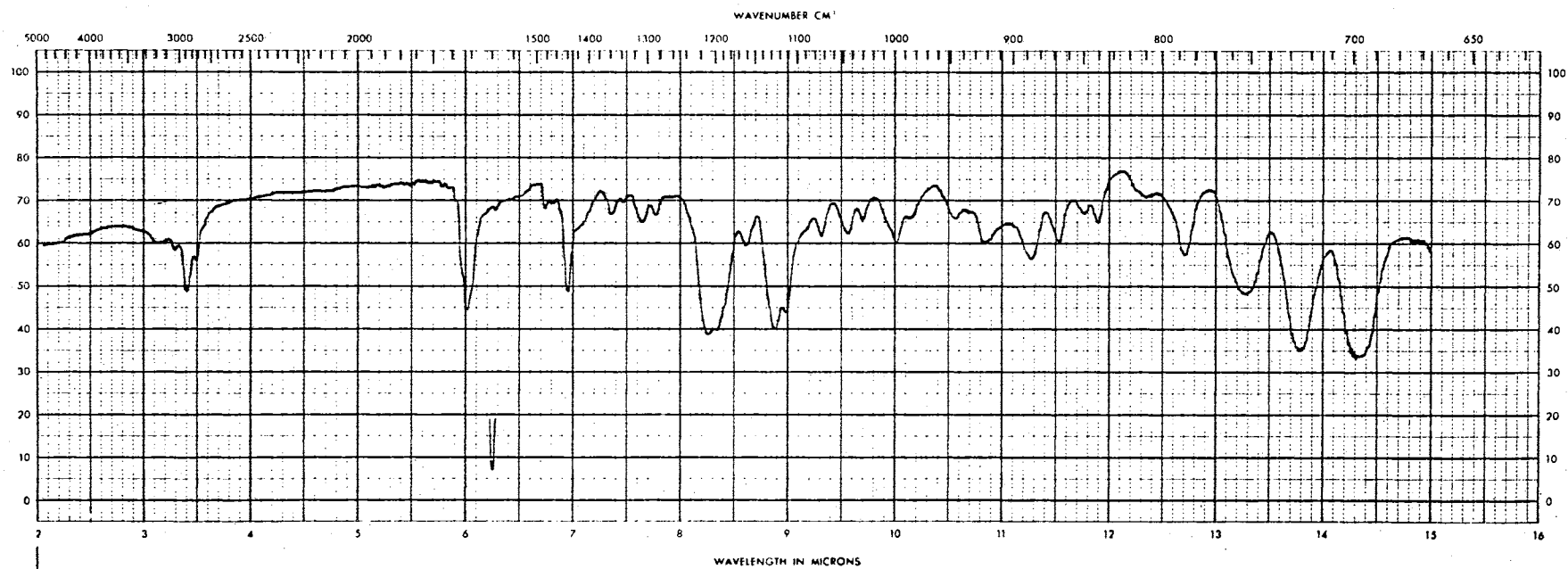
Diethyl Phosphorazidate (I), Film on NaCl Plates.

Plate IX



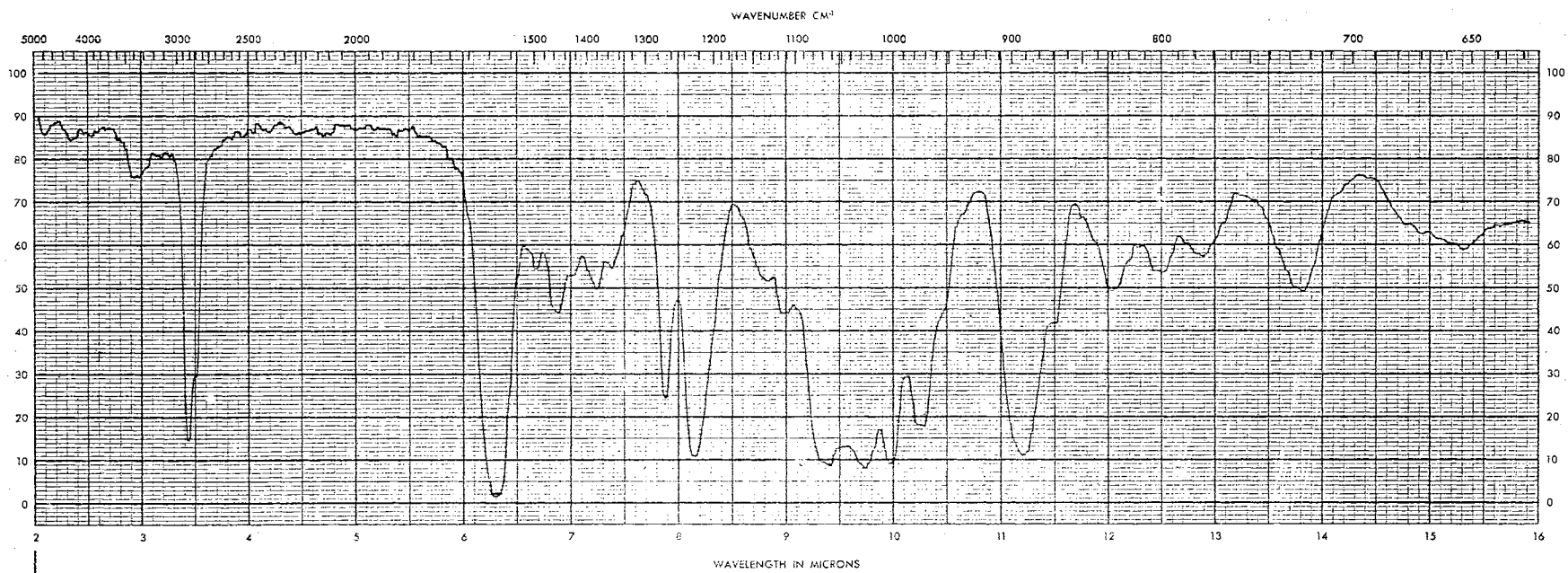
Diethyl 2-Norbornylidene phosphoramidate (V), Film on NaCl Plates.

Plate X



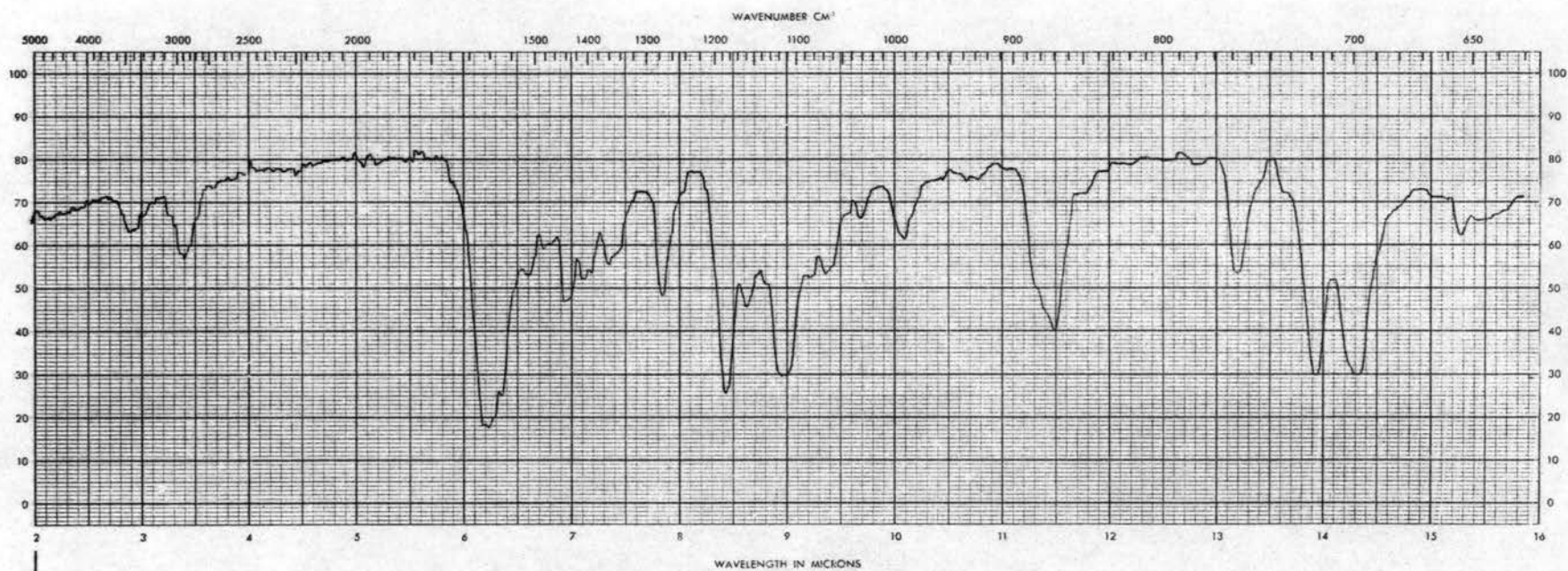
2-Norbornylidene-P,P-diphenylphosphinic Amide (XLIV), Film on NaCl Plates.

Plate XI



N-(Di-n-butylphosphoryl)-N',N'-dimethylisobutyramidine (LXIc), Film on NaCl Plates.

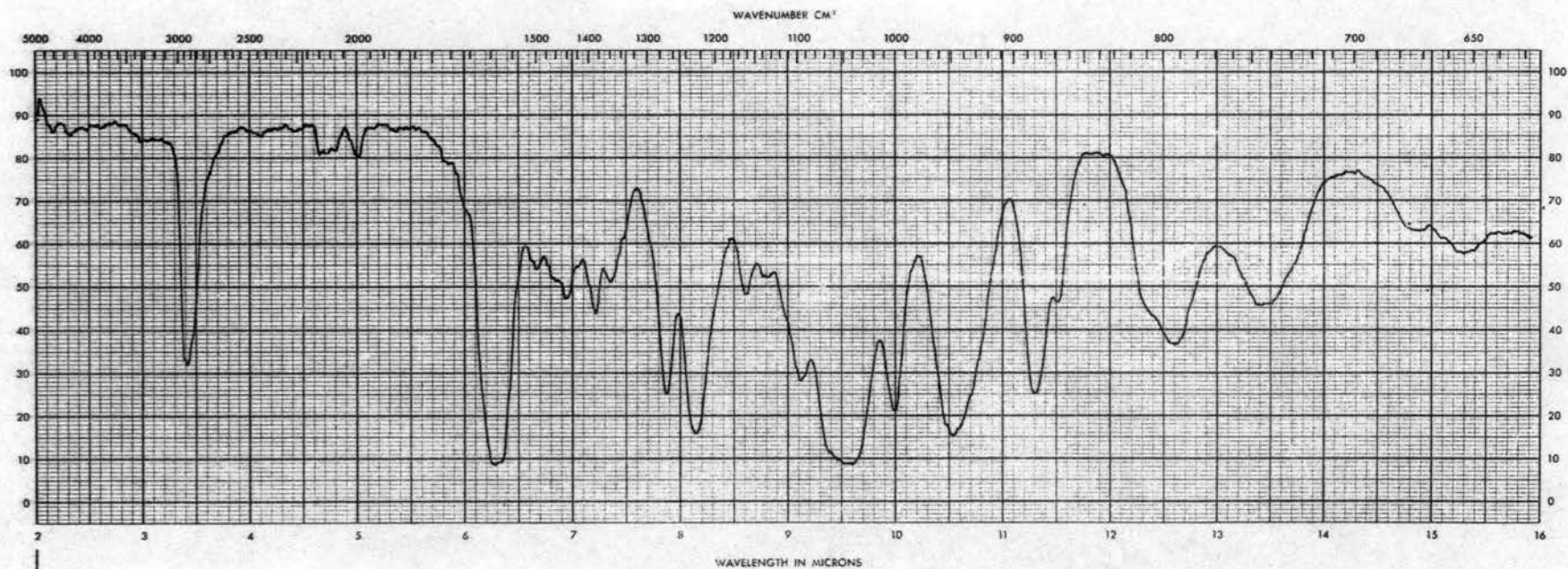
Plate XII



N-(P,P-Diphenylphosphinyl)-N',N'-dimethylisobutyramidine (LXIb), Film on NaCl Plates.

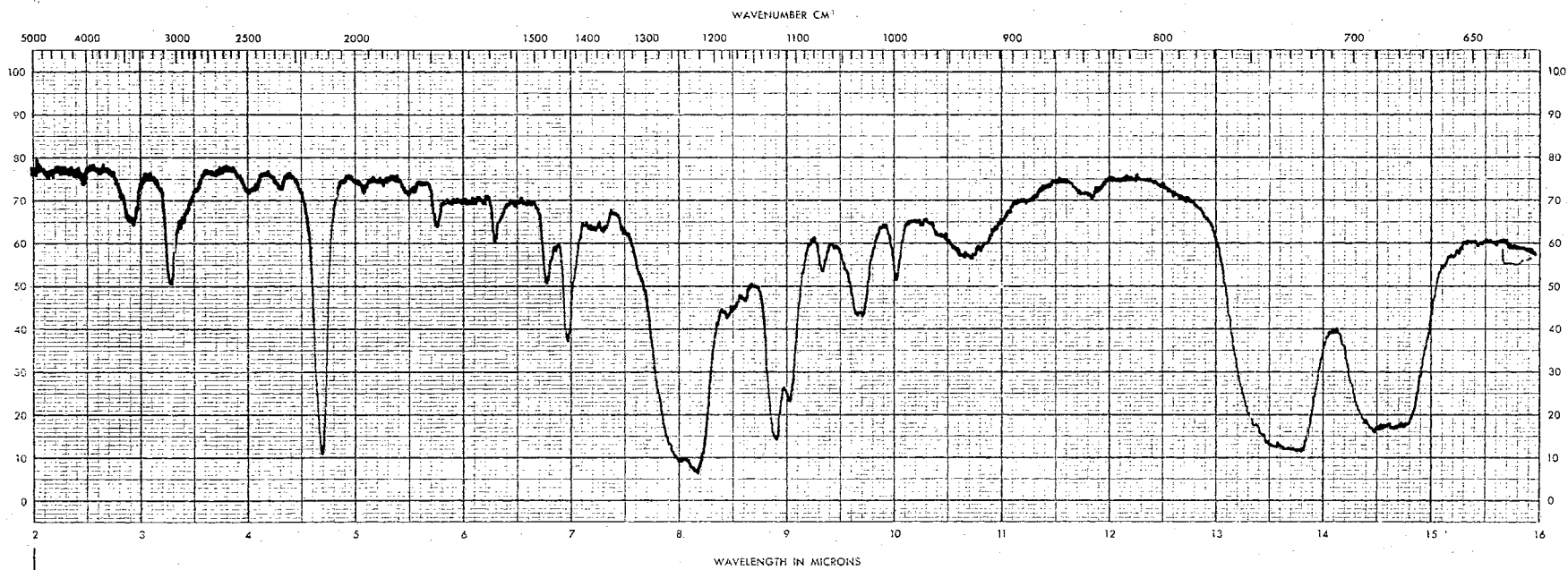


Plate XIII



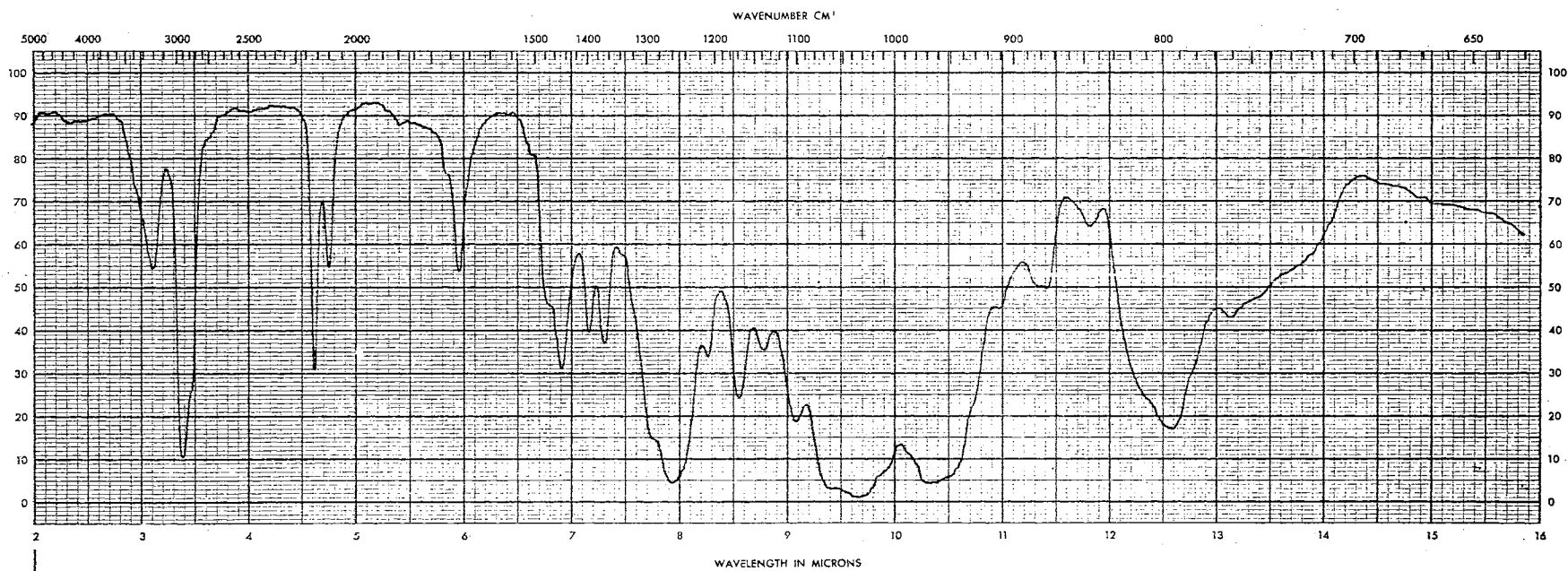
N-(Diethylphosphoryl)-N',N'-dimethylisobutyramidine (LXIa), Film on NaCl Plates.

Plate XIV



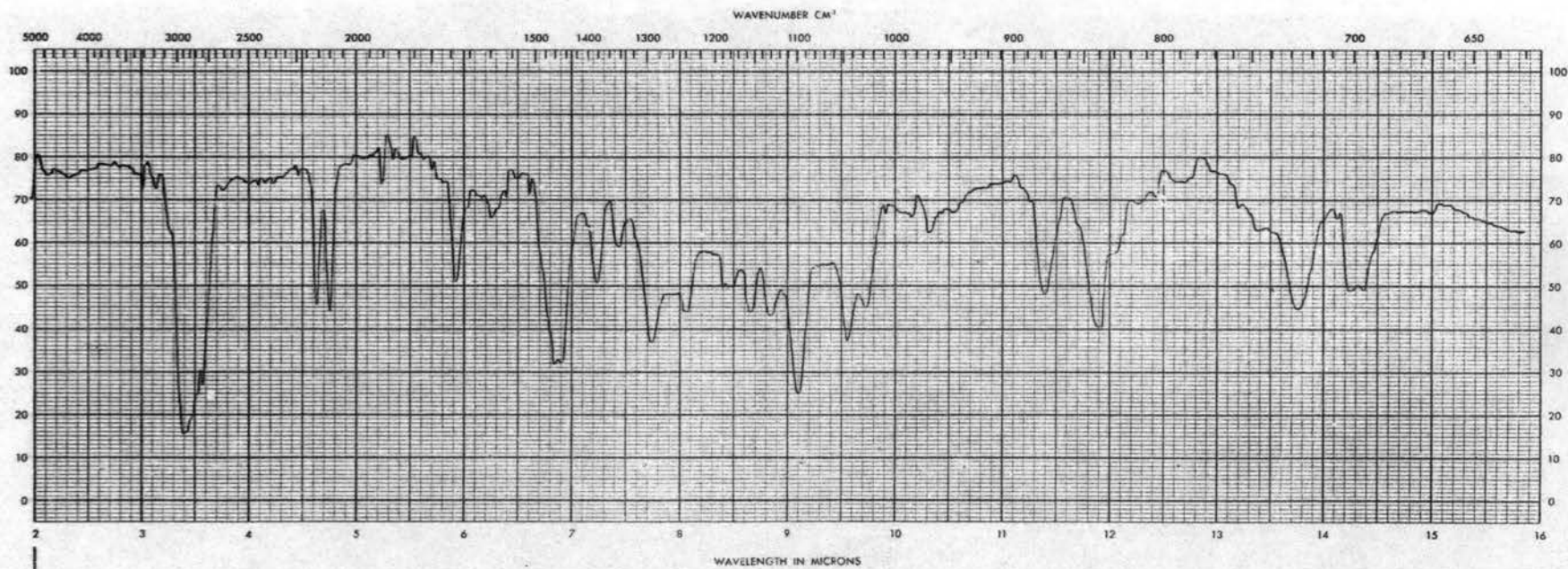
Diphenylphosphinyl Azide (VI), Film on NaCl Plates.

Plate XV



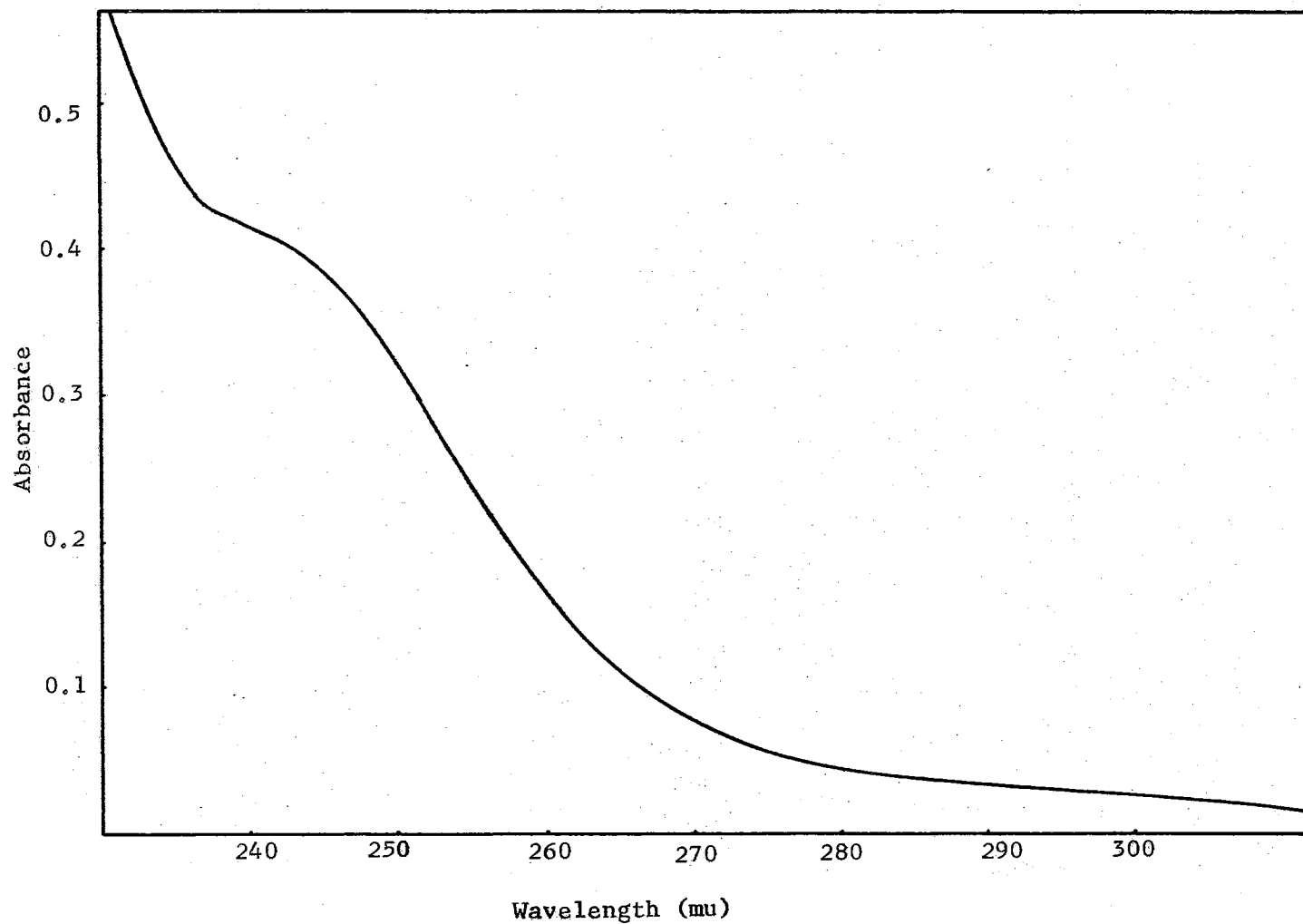
Reaction Mixture of Norbornylene (II), Azide I and Triazoline III, Film on NaCl Plates.

Plate XVI



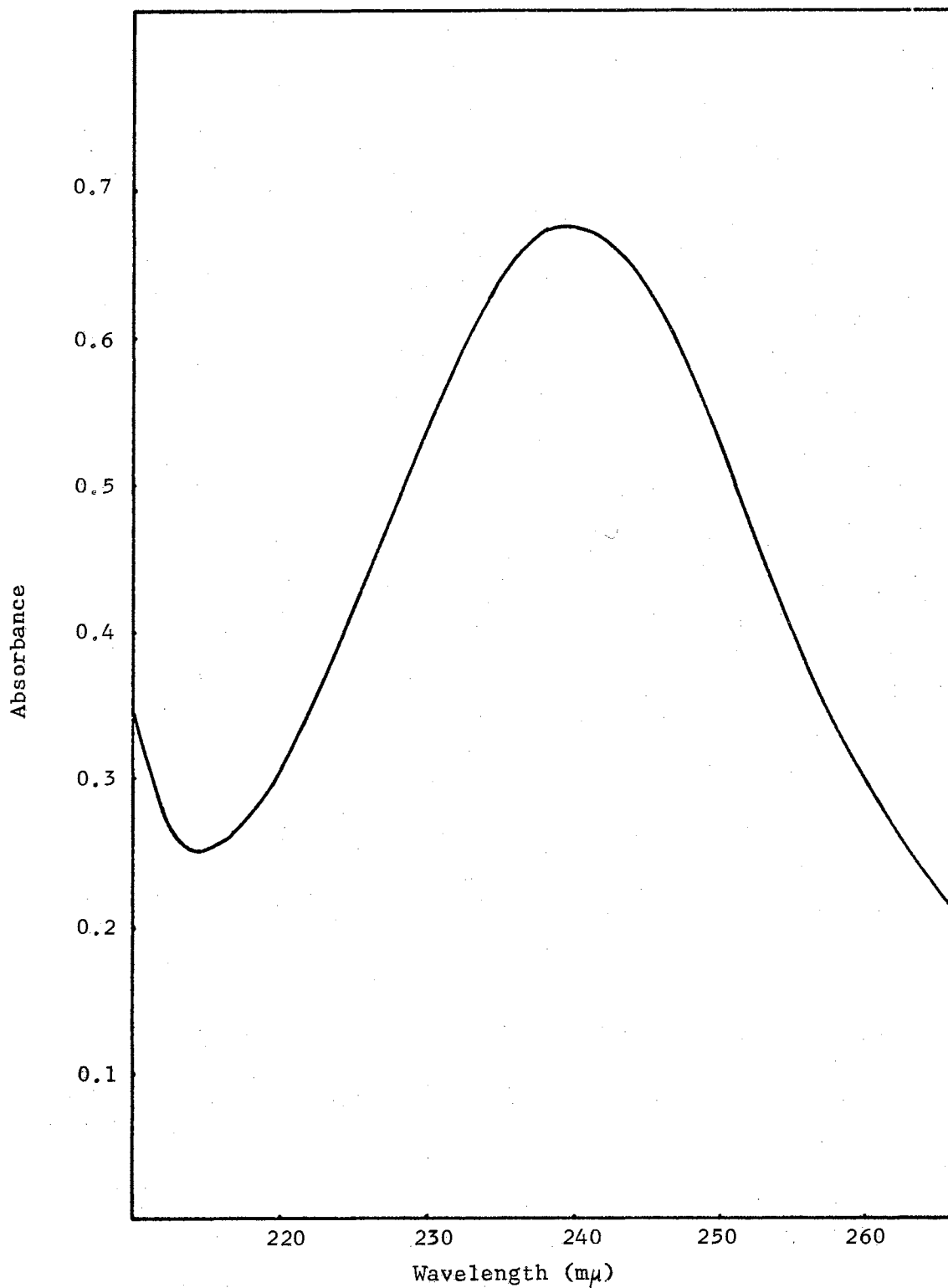
Reaction Mixture of Diphenylphosphinyl Azide (VI) and N,N-dimethylisobutenylamine (XLIX),  
Film on NaCl Plates.

Plate XVII



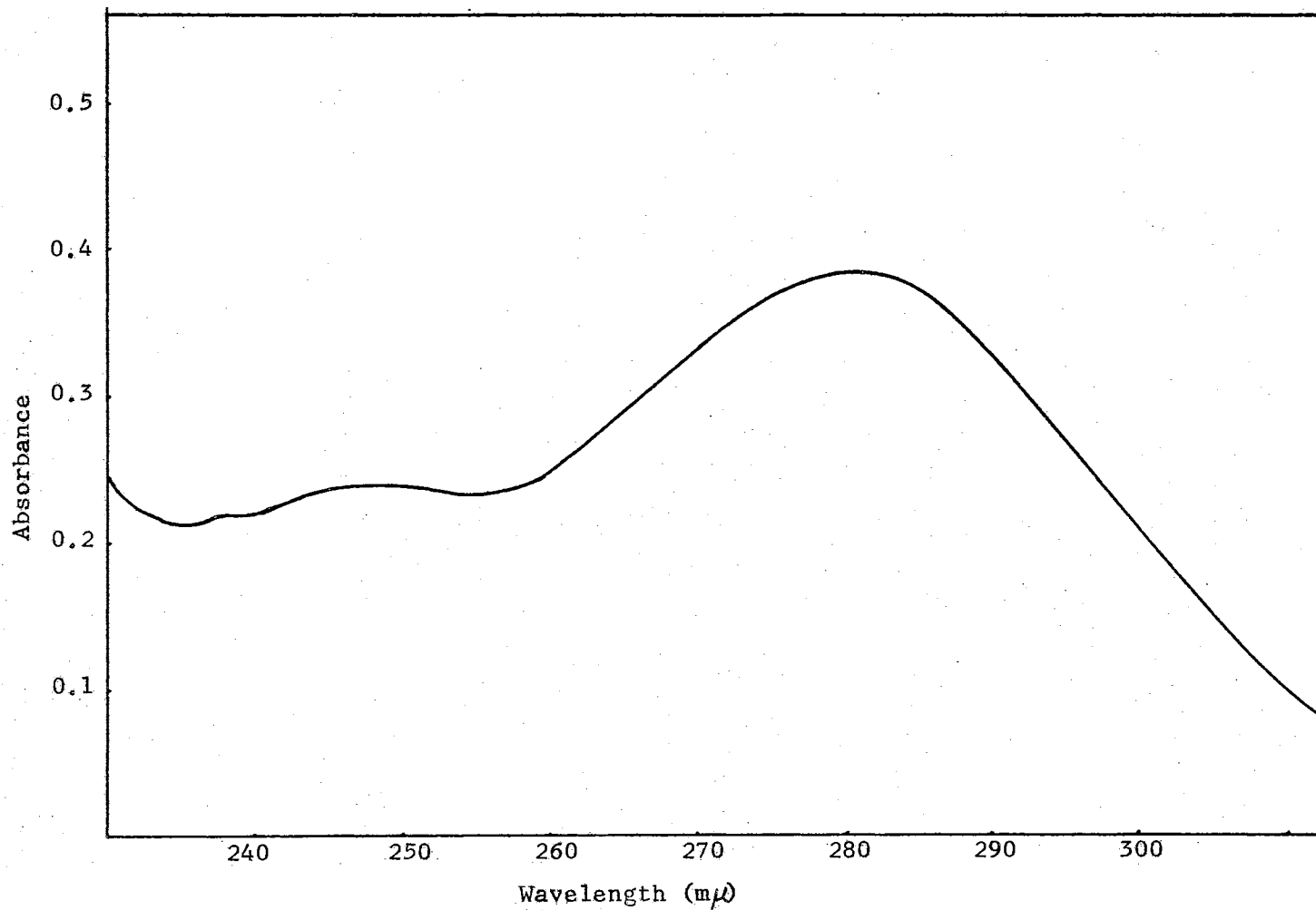
Ultraviolet Spectrum of Diethyl Phosphorazidate (I)  $1.168 \times 10^{-2}$  Molar (Cyclohexane).

## Plate XVIII



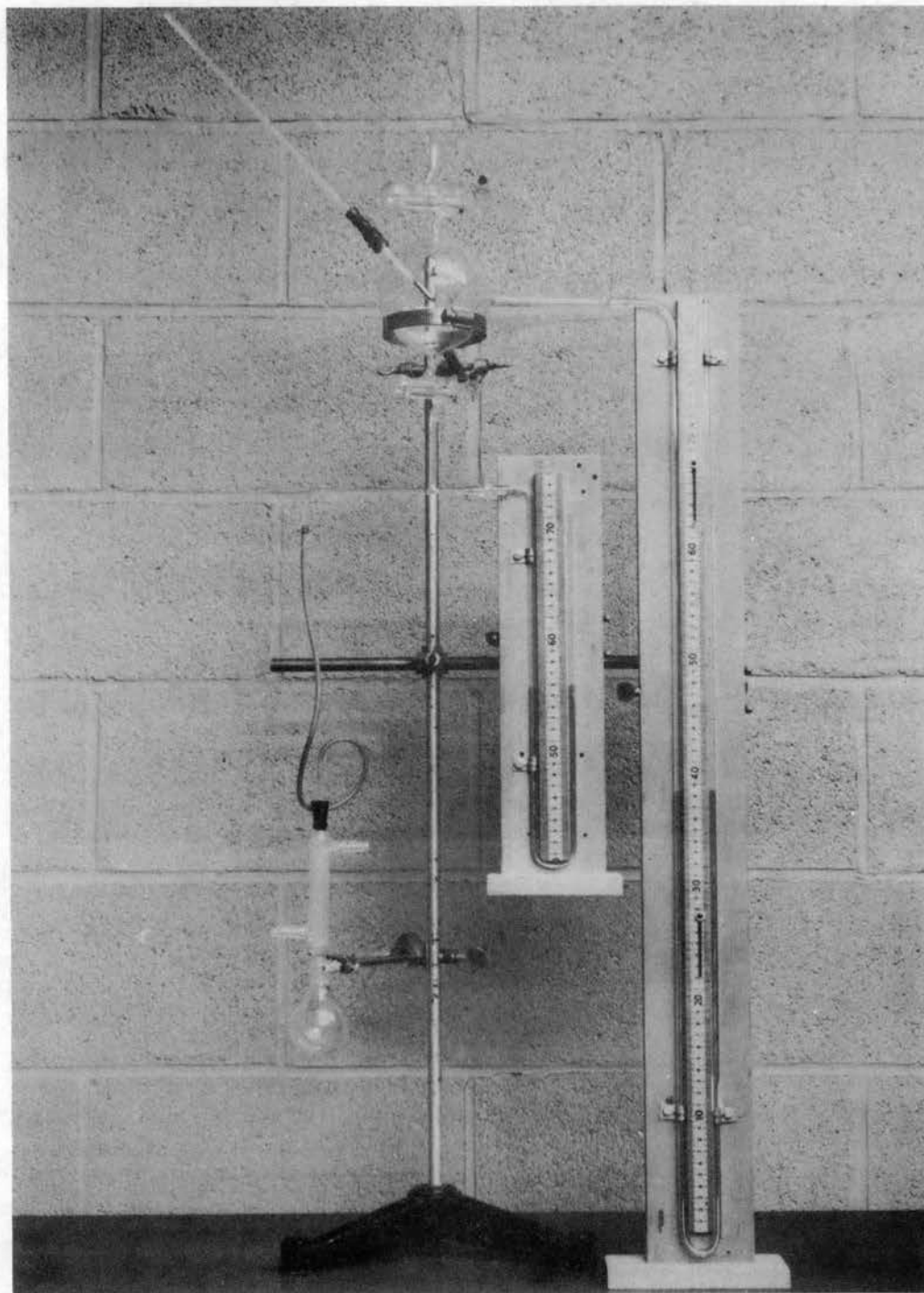
Ultraviolet Spectrum of Diethyl (3a,4,5,6,7,7a-hexahydro-4,7-methano-1H-benzotriazol-1-yl)phosphonate (III),  $1.19 \times 10^{-4}$  molar.  
(Cyclohexane)

Plate XIX



Ultraviolet Spectrum of Diethyl 2-Norbornylidene Phosphoramidate (V),  $5.62 \times 10^{-2}$  molar (Cyclohexane).

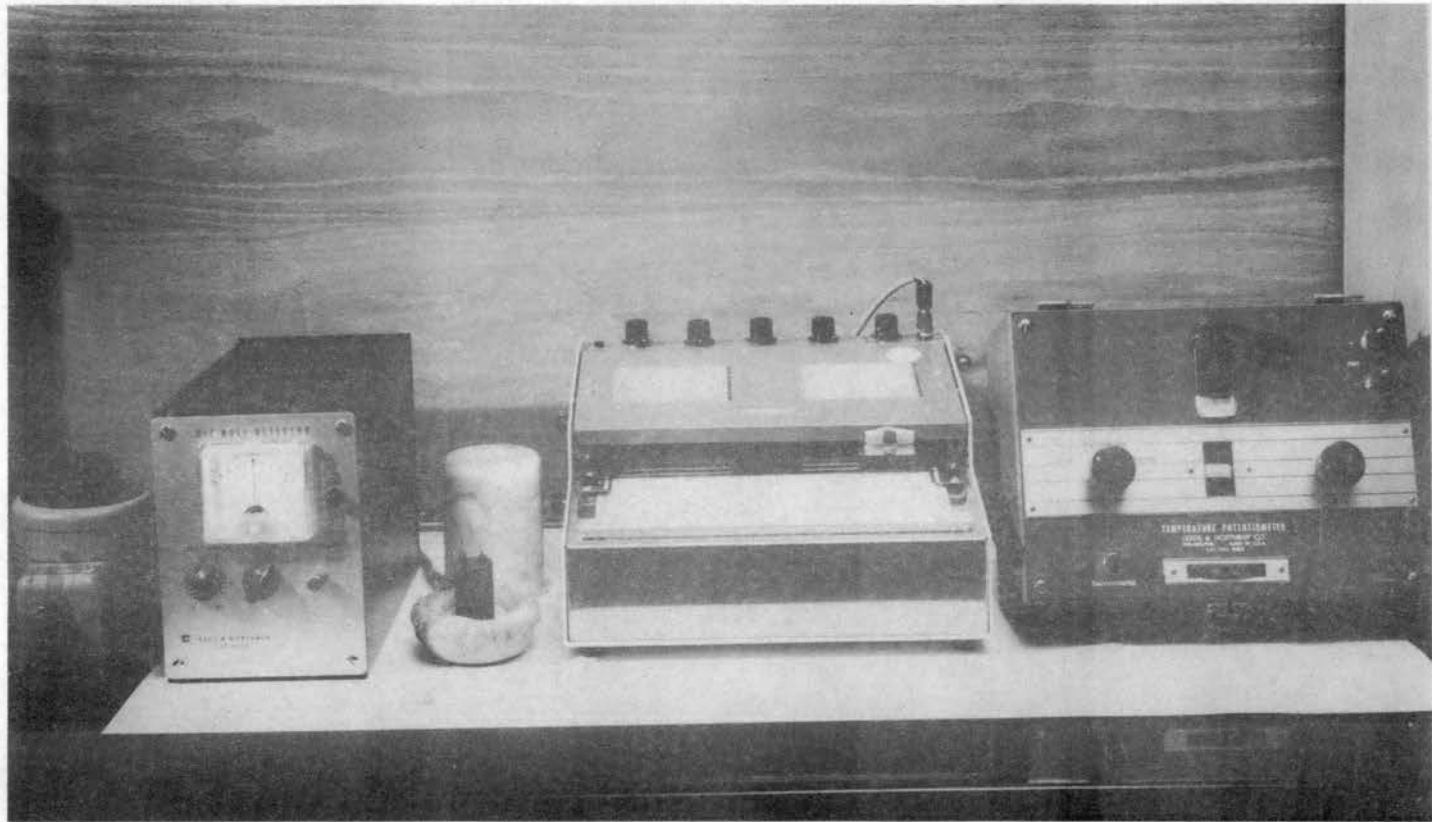
## Plate XX



Apparatus for Measurement of Nitrogen Evolution  
by Conventional Methods



Plate XXI



Differential Thermal Analysis Apparatus

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## VITA

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Candidate for the Degree of

Doctor of Philosophy

**Thesis:** REACTIONS OF PHOSPHORUS AZIDES WITH NORBORNYLENE AND N,N-DIMETHYL-2-METHYLPROPENYLAMINE. A KINETIC STUDY OF THE REACTION OF DIETHYL PHOSPHORAZIDATE WITH NORBORNYLENE

**Major Field:** Organic Chemistry

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