

PYROLYSIS OF AZOALKANES. PART I. SECONDARY

α -DEUTERIUM ISOTOPE EFFECTS. PART II.

RING DEUTERIUM ISOTOPE EFFECT FOR

1,1'-DI(PHENYL-2,3,4,5,6-d₅)-

AZOETHANE

By

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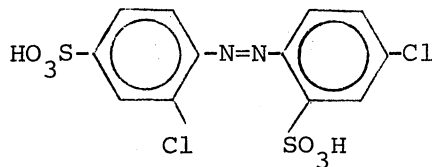
PYROLYSIS OF AZOALKANES. PART I. SECONDARY

α -DEUTERIUM ISOTOPE EFFECTS

CHAPTER I

INTRODUCTION

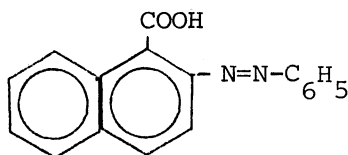
Azo compounds contain alkyl, aryl or alkoxy carbonyl groups attached to the azo group, $-N=N-$, and have the general formula $R-N=N-R'$. If the group R and R' are the same, the compound is usually named by a scheme in which azo is prefixed to the name of the compound from which the groups are derived, e.g. $CH_3-N=N-CH_3$ is azomethane, $C_6H_5-N=N-C_6H_5$ is azobenzene and $C_2H_5O_2CC(CH_3)_2-N=N-C(CH_3)_2CO_2C_2H_5$ is diethyl azoisobutyrate. If the groups are different, the larger one is considered to generate the parent and the other is cited as a prefix with azo, e.g. $C_6H_5-N=N-CH_3$ is (methylazo)benzene. This system suffices for the simpler compounds but soon breaks down for the complex aromatic members of the class. In these, substituents are denoted in the usual way by prefixes and suffixes. The azo group has priority for the lowest available numbers. One set of locants is distinguished by primes, e.g.



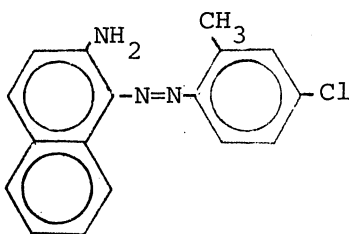
is named 2',4-dichloroazobenzene-2,4'-disulfonic acid. When locants are needed to indicate the position of the azo group they are placed next to the affix "azo" and between it and the name of the molecule to which

each respectively refers. Preference is given to the more complex parent molecule for citation as the first component. All substituents in the component named first are denoted by prefixes unless their presence is indicated in the trivial or semi-trivial name of that component. Locants for substituents in the first-named component are not primed; the others are primed.¹

Examples:



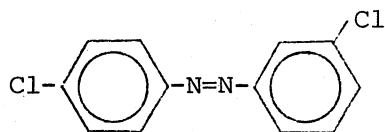
1-Carboxynaphthalene-2-azobenzene



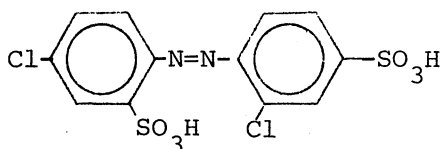
2-Aminonaphthalene-1-azo-(4'-chloro-2'-methyl)benzene

The above described method is prescribed by the International Union of Pure and Applied Chemistry. This older method has yielded to the equally acceptable Chemical Abstracts alternative method.² In the Chemical Abstracts method two principles apply: a) one component is chosen as parent which is regarded as substituted by R-N=N-, this group R being named as a radical: or b) the nomenclature is that for assemblies of identical units with "azo" as a bivalent linking group.

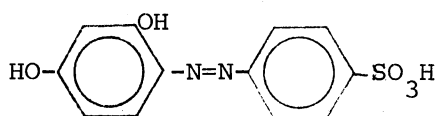
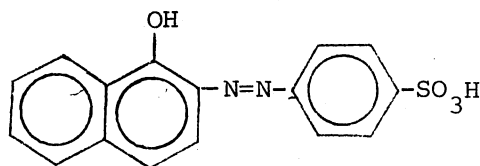
Examples:



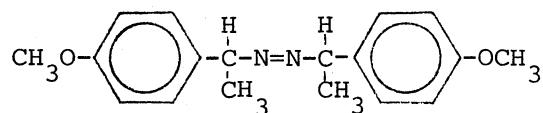
3,4'-Dichloroazobenzene



3',5-Dichloro-2,4'-azodibenzenesulfonic acid

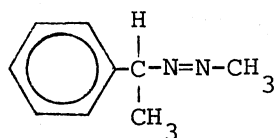
p-(2,4-Dihydroxyphenylazo)benzenesulfonic acidp-(1-Hydroxy-2-naphthylazo)benzenesulfonic acid

Chemical Abstracts in 1973 have begun naming and indexing compounds with the general formula of $R_1-N=N-R_2$ as diazene derivatives.³ The R groups are named as radicals substituted on $H-N=N-H$, e.g.



Bis[1-(4-methoxyphenyl)ethyl]diazene

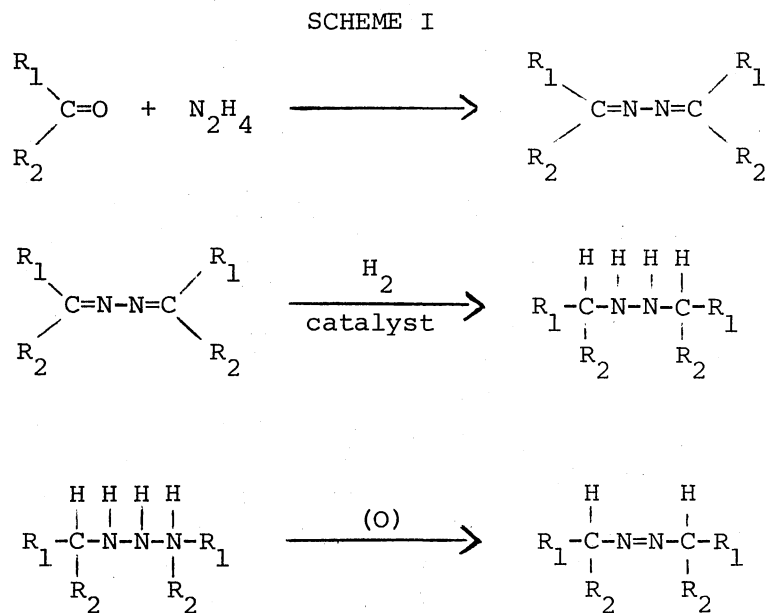
rather than 1,1'-(4,4'-dimethoxy)diphenylazoethane and



1-Methyl-2-(1-phenylethyl)diazene

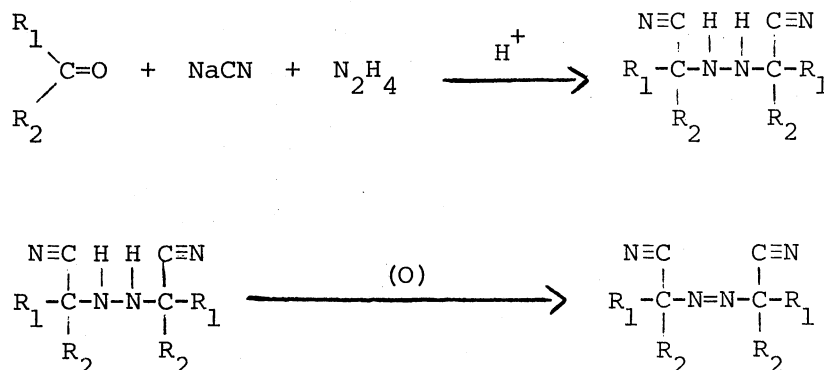
rather than 1-phenylethylazomethane. This newer method for indexing by Chemical Abstracts has not been accepted by most authors in the primary literature⁴, and this discussion the Chemical Abstracts alternate method will be utilized.²

Azo compounds can be divided into three basic classes: 1) those in which one group is aliphatic and the other aromatic, 2) those in which both groups are aromatic and 3) those in which both groups are aliphatic.⁵ The following discussion will restrict itself to the aliphatic azo compounds (mainly symmetrical ones). The most widely used method of preparation of secondary aliphatic azo compounds is the oxidation of 1,2-dialkylhydrazines, which is shown in Scheme I.



The oxidants commonly used are mercuric oxide, hydrogen peroxide, potassium dichromate, cupric salts, nitric acid and bromine water.⁶ The synthetic difficulties associated with Scheme I are: a) synthesis of ketazines may be hindered by poor reactivity of the ketone and slowness of the ketone-hydrazine adduct to eliminate two molecules of water, b) catalytic hydrogenation⁷ of the ketazines may be hampered by steric requirements of the catalyst and complicated by hydrogenolysis of the hydrazine and c) the oxidation of the hydrazine may be slow or the azo compound product may undergo tautomerization. A variation of Scheme I has been utilized by Overberger and coworkers⁸ to synthesize α, α' -dicyano symmetrical azo compounds, Scheme Ia. Scheme Ia does not present the problems of tautomerization during oxidation and reduction processes involved in Scheme I.

SCHEME Ia



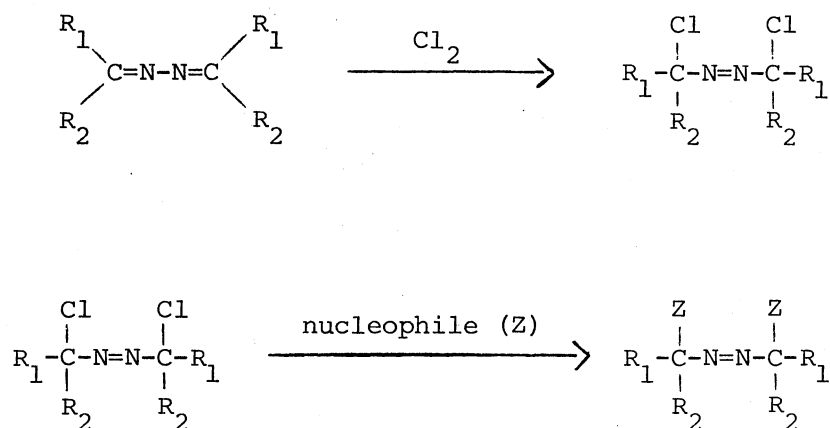
Primary amines may be treated with iodine pentafluoride to oxidize them to symmetrical tertiary aliphatic azo compounds,⁹ Scheme II.



The disadvantages associated with Scheme II are that it requires primary amines with a tertiary α -carbon and it can be used only for the synthesis of tertiary azo compounds.

Synthesis of azo compounds containing various substituents at the α -carbon has been effected by use of α, α' -dichloroazoalkanes (Scheme III).¹⁰ α, α' -Dichloroazoalkanes are prepared by addition of chlorine to

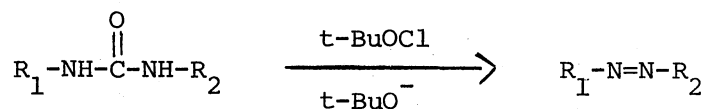
SCHEME III



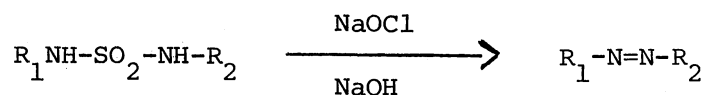
ketazines. The nucleophiles that have been utilized in Scheme III are RCOO^- , RS^- , N_3^- , I^- , RO^- , CN^- , and R^- .¹⁰

Other methods for synthesis of aliphatic azo compounds are: a) treatment of dialkylureas with tert-butyl hypochlorite and tert-butoxide (Scheme IV), b) treatment of alkylated sulfamides with sodium hypochlorite and sodium hydroxide (Scheme V), c) oxidation of alkylated semicarbazides with a copper(II) halide (Scheme VI) and d) hydrolysis, decarboxylation and copper(II) chloride oxidation of N,N'-dialkylated diethyl 1,2-hydrazinedicarboxylates (Scheme VII).¹¹ Schemes IV through

SCHEME IV

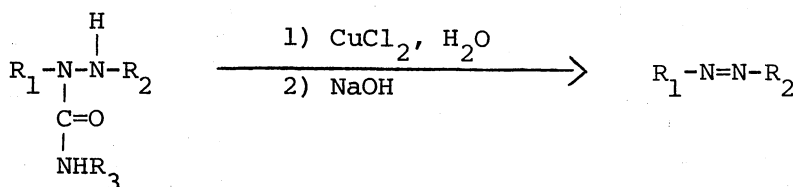


SCHEME V

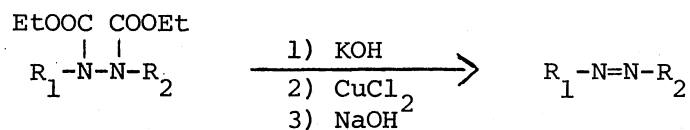


VII present similar synthetic difficulties: a) all utilize strong base which increases the probability of tautomerization of secondary azo compounds and b) each has only been utilized to a very limited extent,

SCHEME VI



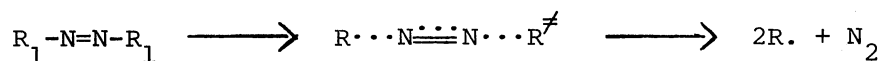
SCHEME VII



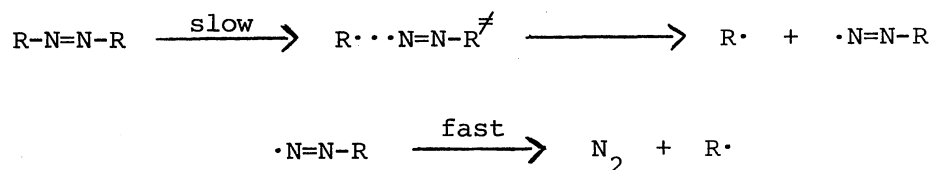
in the synthesis of either unsymmetrical or bicyclic azo compounds.

Azo compounds decompose thermally. The ease of decomposition varies with the expected stability of the incipient free radicals.^{6b} The possibility of either simultaneous carbon-nitrogen bond rupture, Scheme VIII, or stepwise carbon-nitrogen bond rupture, Scheme IX, has been discussed by several workers.

SCHEME VIII



SCHEME IX



Ramsperger¹² studied the rates of gas-phase decomposition of azo-methane (I), 2-(methylazo)propane (II), and 1,1'-dimethylazoethane (III). The temperature dependence of the rate constant values yields activation energies of 51.2, 47.5 and 40.9 kilocalories per mole, respectively. For a one-step decomposition mechanism (Scheme VIII), Ramsperger suggested that the activation energy for II should be the

average of the activation energies of I and III. From these data, the decomposition is qualitatively via Scheme VIII. Cohen and Wang^{7a,13} and Overberger and DiGiulio¹⁴ have compared the activation energies and rates of decomposition for III, 1-methyl-1'-phenylazoethane (IV) and 1,1'-diphenylazoethane (V) in an attempt to decide whether compound V decomposes via Scheme VIII or IX (Table I).

TABLE I

RATE OF DECOMPOSITION AND ACTIVATION PARAMETERS FOR THE THERMOLYSIS OF III, IV, AND V AT 120°C¹⁴

Compound	$k \times 10^4, \text{sec}^{-1}$	$E_a, \text{kcal/mole}$	$\Delta S^\ddagger, \text{e.u.}$
<u>III</u> ^a	0.00001	40.9	1
<u>IV</u> ^b	0.132	36.5	9.3
<u>V</u> ^c	4.85	32.6	7

^aDecomposed in the vapor phase extrapolated to 120°C.

^bDecomposed in diphenyl ether extrapolated to 120°C.

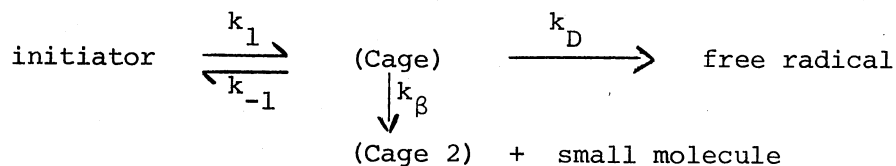
^cDecomposed in ethylbenzene.

It is observed that replacement of a methyl group in III by a phenyl in IV causes a decrease of approximately four kilocalories in the activation energy (E_a) and symmetrical replacement of a pair of methyls in III by a pair of phenyls in V gives an approximate decrease in E_a of eight kilocalories. Compound IV is approximately ten thousand times as reactive as III, which is a result of a decrease in E_a and the

increase in ΔS^\ddagger . Replacement of a methyl group in IV by a phenyl group to arrive at V causes only a thirty-seven fold increase in reactivity. This appears to be due to the fact that the entropy of activation remains almost constant. The rate of decomposition of IV and V should be approximately of the same order except for a statistical factor of two, if V decomposed via Scheme VIII. Therefore, V decomposes via Scheme VIII.^{13,14}

Pryor and Smith¹⁵ have developed a relationship between the viscosity dependence of the observed rate constant (k_{obs}) for decomposition of a free radical initiator and the number of bonds which undergo scission in the decomposition of the initiator. Scheme X describes the decomposition of a free radical initiator.

SCHEME X



The observed rate constant for Scheme X is given in Equation 1, when k_β is zero or where k_β/k_D can be neglected relative to unity.

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 A_D} \left(\frac{\eta}{A_V} \right)^\alpha \quad (1)$$

Equation 1 predicts a linear relationship between $1/k_{\text{obsd}}$ and $(\eta/A_V)^\alpha$,

where \tilde{A}_D is the Arrhenius parameter for diffusion, \tilde{A}_V is the constant of viscosity for each solvent, η is the viscosity and α is believed to be dependent upon the type of solvent (i.e. unbranched aliphatic hydrocarbons), temperature, and size and shape of the geminate radicals.^{15,16}

Pryor and Smith observed such a correlation for a wide variety of experimental data where α is set equal to 0.5. Qualitatively Equation 1 allows initiators to be divided into two classes; multibond initiators give no cage return and have k_{-1} equal to zero and one-bond initiators give cage return and have finite k_{-1} values. This separation of initiators into two classes is based on the following postulates: 1) Any molecule that decomposes by the synchronous scission of two or more bonds breaks into too many pieces to allow cage return; such decompositions will have rate constants that are independent of the solvent viscosity. 2) Any molecule that decomposes by scission of only one bond can give cage return in solution by a simple radical recombination. For such a molecule the observed rate constant for decomposition will decrease as the viscosity of the solvent increases since fewer geminate pairs will separate at higher viscosities and more will undergo cage return. The following four requirements must be met before this test may be applied:

- 1) All the rate constants except k_D either must remain invariant as the viscosity of the system is changed or the changes in them must be small compared to the change in k_D .
- 2) It must be possible to change the solvent viscosity in such a way as to keep the solvating power of the solvent essentially constant.
- 3) The change in the measured macroscopic viscosity of the solvent must parallel the change in the diffusive barrier experienced by molecular species.
- 4) The lifetime of the radicals produced by the initial bond homolysis must be at least of the same

order of magnitude as the time required for diffusive separation of the geminate pair.¹⁵

Pryor and Smith have applied the viscosity test to 2,2'-diphenyl-2,2'-azopropane (VI) and (p-nitrophenylazo)triphenylmethane (VII). The data for the decomposition of VI and VII are shown in Figure I. The plot of Equation 1 for the decomposition of VI shows that k_{obsd} is independent of solvent viscosity.¹⁵ This result is in agreement with the conclusion of Nelsen and Bartlett^{9b} that VI decomposes via Scheme VIII. The plot of Equation 1 for the decomposition of VII shows that k_{obsd} decreases regularly as the solvent is changed from low-molecular-weight high-viscosity solvents to high-molecular-weight high-viscosity solvents.¹⁵ This is evidence that VII decomposes by the initial scission of only one carbon-nitrogen bond, which is consistent with the results of Cohen and Wang.¹⁷

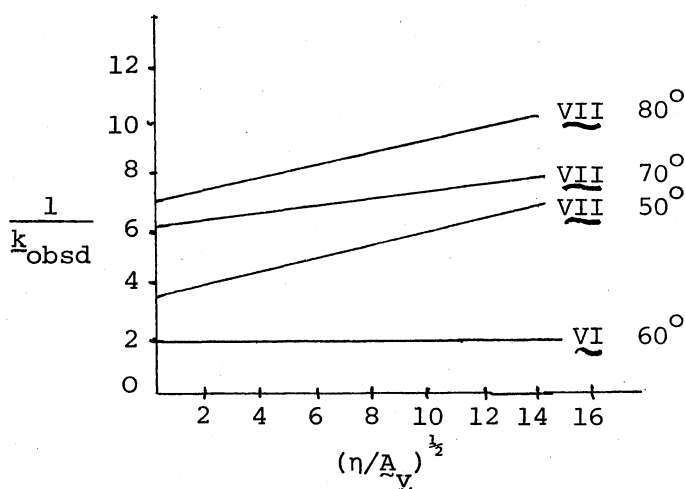
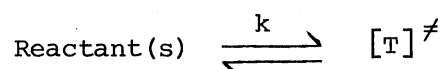


Figure 1. The Observed Rate Constants for Pyrolysis of VI and VII as a Function of Solvent Viscosity¹⁵

Another approach to the problem of the mechanism of azo compound pyrolysis is measurement and analysis of kinetic isotope effects. The basic assumption which underlies theoretical consideration of isotope effects is the Born-Oppenheimer approximation.¹⁶ This approximation states that the interatomic electronic forces are independent of nuclear masses. Thus the potential energy surface describing the motions of the nuclei is independent of isotopic substitution. The mechanism of a chemical reaction is independent of isotopic substitution. The rates of reaction of isotopic reactants will differ in magnitude depending almost entirely on the changes in interatomic electronic forces occurring as the reaction proceeds. In the transition-state formulation, a single reaction step may be represented as Scheme XI where T^\ddagger is the transition state. The transition state may be thought of as the highest point along the path of least expenditure of energy in passing from reactant(s) to product(s) on the potential energy surface for a given reaction. The rate constant, k , for this reaction step (Scheme XI) is given by

SCHEME XI



Equation 2, where k is Boltzmann's constant, h is Planck's constant, T is the absolute temperature, Q_T^\ddagger is the partition function of the transition state with the degree of freedom corresponding to the reaction coordinate omitted, Q_n is the complete statistical-mechanical partition function for the reactant(s) and the transmission coefficients κ is normally assumed to be one.¹⁶

$$k = \kappa \frac{kT}{h} \frac{Q_T^\ddagger}{Q_n} \quad (2)$$

The isotopic rate constant ratio, k_1/k_2 , is given by Equation 3,

$$\frac{k_1}{k_2} = \frac{\frac{Q_2}{Q_1}}{\frac{Q_2^\ddagger}{Q_1^\ddagger}} \quad (3)$$

where the subscripts 1 and 2 designate the light and heavy isotopic species. Substitution of the expressions for the translational, rotational and vibrational partition function contributions gives Equation 4, where MMI is the mass moment of inertia term which arises from the classical translational and rotational partition functions, EXC contains vibrational frequencies ($u = hv/kT$, v = normal mode vibrational frequency) and arises from the thermal excitation of vibrations, and ZPE is the total difference between reactant and transition state zero-point energies for labeled and unlabeled systems.¹⁸ Equation 5 may be derived from Equation 4 by application of the Teller-Redlick product rule,^{18d} where $v_{1L}^\ddagger/v_{2L}^\ddagger$ is the ratio of the imaginary frequencies for motion parallel to the reaction

$$\frac{k_1}{k_2} = \frac{\left(\frac{M_2}{M_1}\right)^{\frac{3}{2}} \left(\frac{I_{R2}}{I_{R1}}\right)^{\frac{1}{2}}}{\left(\frac{M_2^\ddagger}{M_1^\ddagger}\right)^{\frac{3}{2}} \left(\frac{I_{R2}^\ddagger}{I_{R1}^\ddagger}\right)^{\frac{1}{2}}} \quad (4)$$

$$\begin{aligned}
 & \prod_{i=1}^{3N-6} \frac{(1 - \exp(-u_{ii}))}{(1 - \exp(-u_{2i}))} \\
 \times & \prod_{i=1}^{3N-7} \frac{(1 - \exp(-u_{11}^{\neq}))}{(1 - \exp(-u_{21}^{\neq}))}
 \end{aligned}$$

$$\times \frac{\exp \sum_{i=1}^{3N-6} (u_{ii} - u_{2i})/2}{\exp \sum_{i=1}^{3N-7} (u_{ii}^{\neq} - u_{2i}^{\neq})/2}$$

or

$$\frac{k_1}{k_2} = (\text{MMI}) \times (\text{EXC}) \times (\text{ZPE})$$

coordinate at the transition state for the isotopic molecules and VP is the vibrational product term.^{18a}

$$\frac{k_1}{k_2} = \frac{v_{1L}^{\neq}}{v_{2L}^{\neq}} \times (\text{VP}) \times (\text{EXC}) \times (\text{ZPE}) \quad (5)$$

Equation 5 is usually called the Bigeleisen formulation.^{18b} $v_{1L}^{\neq}/v_{2L}^{\neq}$ is termed the classical mechanical portion and (VP) (EXC) (ZPE) is termed the quantum mechanical portion. Wolfsberg and Stern¹⁸ have shown that isotope effects are a result of force constant changes associated with isotopic nuclei upon passing from reactant state to the transition state. A tendency toward smaller force constants for isotopic nuclei in the transition state than in the reactant yields a $k_{\text{H}}/k_{\text{D}}$ greater than one (ZPE < 0), and a tendency toward greater force constants yields a $k_{\text{H}}/k_{\text{D}}$ less than one (ZPE > 0).¹⁹

Kinetic isotope effects are useful tools in elucidating reaction mechanisms. The measurement of a sufficient number of isotope effects increases the information about the potential-energy reaction hypersurface. By studying the isotope effects for a series of structurally related compounds undergoing a given reaction, it should be possible to obtain an understanding of the effects of changes in the reactant structure upon reactivity.²⁰

Isotope effects have been used to study the thermal decomposition of azo compounds. Alpha-deuterium, primary nitrogen, and primary carbon isotope effects for the thermal decomposition of V,²¹ IV²² and VIII²³ are tabulated in Table II.

TABLE II
ISOTOPE EFFECTS AND ACTIVATION ENERGIES FOR THERMAL
DECOMPOSITION OF V, IV AND VIII⁷

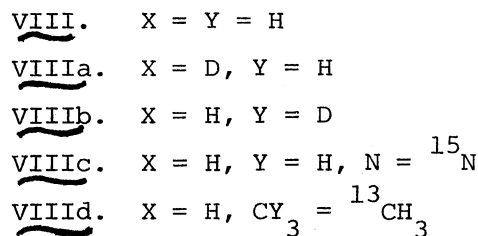
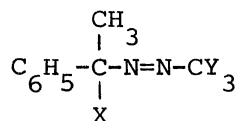
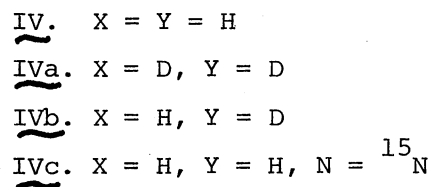
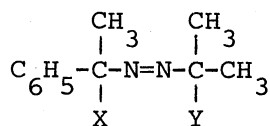
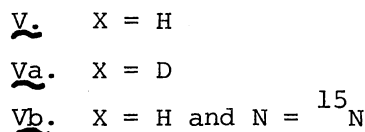
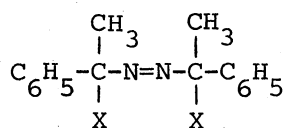
Compound	T, °C	k_H/k_D per \underline{D}	Position of \underline{D}	k_{14}/k_{15}	E_a , kcal/mole
<u>V</u>	105.28	1.127	benzyl	1.0229	32.6 ^a
<u>IV</u>	143.20	1.148	benzyl	1.0152	36.5 ^b
		1.036	propyl		
<u>VIII</u>	161.00	1.13	benzyl	1.0132	38.6
		0.97	methyl		
<u>VIII</u>			methyl	$k_{12}/k_{13} =$	1.0068

^aSee reference 13.

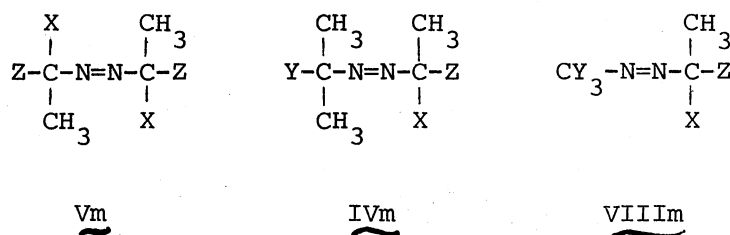
^bSee reference 14.

These data are indicative of a change in mechanism from simultaneous carbon-nitrogen bond rupture for V (see Scheme VIII) to stepwise carbon-nitrogen bond rupture for VIII (see Scheme IX).²³ The α -effects indicate that as the molecular dissymmetry is increased the extent of benzylic C-N bond rupture increases and the extent of nonbenzylic C-N bond rupture decreases. The inverse effect observed for deuterium in the methyl position for VIIIb indicates a strengthening of the methyl C-N bond in the transition state.²³ The activation energies lead to generally equivalent conclusions.²⁴ The isotope effects yield both qualitative and quantitative information not obtained from activation energies concerning structure-reactivity relationships.^{19,25}

Seltzer and Mylonakis²⁶ have performed extensive model calculations of primary and secondary deuterium isotope effects for the thermal decomposition of V, IV and VIII.



The cut-off procedure was utilized in the calculation of the isotope effects. The models used were Vm, IVm and VIIIIm for reactants V, IV and VIII, respectively. The phenyl group is designated by a point mass Z of mass 77 amu and X and Y are defined as above. In the transition state of Vm the C-N bond length was increased from 1.47 to 1.71^oÅ and the N=N distance



reduced from 1.24 to 1.17^oÅ. The results of the model calculations are in Table III. The assumed transition state for decomposition of V involves a nearly complete loss of both of the C-N bonds with a weakening of the bending force constants about the central carbons. This model is consistent with both the hydrogen and nitrogen isotope effects.

For pyrolysis of VIII, the transition state force constants and isotope effects they predict are tabulated in Table IV.

The good agreement between the calculated and observed results indicate that: 1) the methyl H-C-N bending force constants increase in the transition state and give rise to the inverse α -(methyl)deuterium isotope effect; 2) the benzylic H-C-N bending force constants decrease which gives a normal α -(benzylic)deuterium effect; 3) the benzylic C-N stretch is essentially lost in the transition state and 4) the transition state is not symmetric as it was for V (Vm). Seltzer and Mylonakis felt that VIIIIma was the most plausible model.

TABLE III

FORCE CONSTANT CHANGES AND CALCULATED ISOTOPE EFFECTS FOR MODEL $\underline{V_m}^{19}$

Bond Involved	Force Constant ^a in		
	Reactant	Transition State	
		$\underline{V_{ma}}$	$\underline{V_{mb}}$
C-N stretch	5.0	2.5	0.1
N=N stretch	10.0	12.5	12.5
H-C-N bend	0.60	0.23	0.23
Z-C-N bend	1.10	0.45	0.45
C-C-N bend	1.10	0.45	0.45
C-N=N bend	1.20	0.45	0.45
\underline{f}_{int}		-2.5001	-0.1001

Rates Involved	Isotope Effects		
	Observed	Calculated	
		$\underline{V_{ma}}$	$\underline{V_{mb}}$
$\frac{k_{\underline{V}}}{k_{\underline{V_a}}}^b$	1.27 ± 0.02	1.269	1.270
$\frac{k_{\underline{V}}}{k_{\underline{V_b}}}$	$1.0022_a \pm 0.001_4$	1.0136	1.0230

^a Force constants are in mdynes/ $\overset{\circ}{A}$.^b For two deuterium.

TABLE IV
FORCE CONSTANT CHANGES AND CALCULATED ISOTOPE EFFECTS FOR VIIIIm¹⁹

Bond Involved	Force Constant ^a in			
	Reactant	<u>VIIIIma</u>	<u>VIIIImb</u>	<u>VIIIImc</u>
C-N stretch (benzylic)	5.0	0.1	0.1	0.0
C-N stretch (methyl)	5.0	5.65	5.0	5.0
N=N stretch	10.0	12.0	13.5	13.5
H-C-N bend (benzylic)	0.60	0.162	0.162	0.162
H-C-N bend (methyl)	0.60	0.69	0.68	0.68
C-N bend	1.10	0.297	0.297	0.297
Z-C-N bend	1.10	0.297	0.297	0.297
C-N=N bend (benzylic)	1.20	0.324	0.324	0.324
C-N=N bend (methyl)	1.20	1.38	1.36	1.36
\bar{f}_{int}		-0.75167	+0.75167	0.0

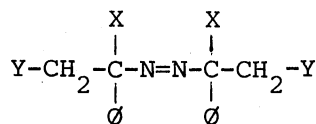
Rates Involved	Isotope Effects			
	Observed	Calculated		
		<u>VIIIIma</u>	<u>VIIIImb</u>	<u>VIIIImc</u>
$\frac{k_{\text{VIII}}}{k_{\text{VIIIa}}}$	1.13 ± 0.01	1.12	1.122	1.120
$\frac{k_{\text{VIII}}}{k_{\text{VIIIb}}}$	0.97 ± 0.01	0.966	0.960	0.968
$\frac{k_{-12}}{k_{-13}}$	1.0068 ± 0.0006	1.0061	1.0030	1.0063
$\frac{k_{-14}}{k_{-15}}$ (average)	1.0132 ± 0.0008	1.0130	1.0138	1.0124

^aForce constants are in mdynes/Å.

The results for model calculations for IV(IVm) are tabulated in Table V. The results for model calculations for IV are consistent with the previous results. The C-N(isopropyl) stretching force constant for IV decreases upon passing to the transition state, but not to the extent that the C-N(benzylic) stretching force constant does. This indicates an unsymmetrical rupture of the C-N bonds in IV as in VIII.

The above calculations indicate the distinct advantage of using models and computers^{25a} as an aid in the interpretation of kinetic isotope effect data.

Alpha-secondary deuterium isotope effects have been used²⁷ to investigate the influences of molecular structure upon the thermal decomposition of symmetrical azo compounds. The α -effects and activation parameters for the thermal decomposition of meso- and dl-1,1',2,2'-tetraphenylazoethane (IX), 1,1'-diphenylazobutane (X) and 2,2'-dimethoxy-1,1'-diphenylazoethane (XI) are tabulated in Table VI.



<u>meso</u> - and <u>dl</u> - <u>IX</u>	Y = \emptyset	X = H
<u>meso</u> - and <u>dl</u> - <u>IXa</u>	Y = \emptyset	X = D
<u>X</u>	Y = CH ₂ CH ₃	X = H
<u>Xa</u>	Y = CH ₂ CH ₃	X = D
<u>XI</u>	Y = OCH ₃	X = H
<u>XIa</u>	Y = OCH ₃	X = D

TABLE V

FORCE CONSTANT CHANGES AND CALCULATED ISOTOPE EFFECTS FOR IVm

Bonds Involved	Force Constant ^a in	
	Reactant	Transition State
C-N stretch(benzylic)	5.0	0.1
C-N stretch(isopropyl)	5.0	4.0
N=N stretch	10.0	12.0
H-C-N bend(benzylic)	0.60	0.126
H-C-N bend(isopropyl)	0.60	0.480
C-C-N bend(benzylic)	1.10	0.232
C-C-N bend(isopropyl)	1.10	0.880
Z-C-N bend	1.10	0.232
C-N=N bend(benzylic)	1.20	0.252
C-N=N bend(isopropyl)	1.20	0.960
f_{int}		-0.63246
Rates Involved	Isotope Effects	
	Observed	Calculated
$k_{\text{IV}}/k_{\text{IVa}}$	1.15 ± 0.01	1.1493
$k_{\text{IV}}/k_{\text{IVb}}$	1.036 ± 0.007	1.0400
k_{14}/k_{15}	1.0152 ± 0.0005	1.0150

^aForce constant units are mdynes/ \AA .

TABLE VI
ISOTOPE EFFECTS AND ACTIVATION ENERGIES FOR THERMAL
DECOMPOSITION OF IX, X AND XI

Compound	Temp. °C	$k_{\underline{H}}/k_{\underline{D}}^a$	E_a (kcal/mole)	$k_{\underline{H}}/k_{\underline{D}}^{a,b}$ 105.28°
meso- <u>IX</u> / <u>IXa</u>	106.47	1.224 ^c	33.1 ^c	1.225
dl- <u>IX</u> / <u>IXa</u>	106.47	1.202 ^c	33.2 ^c	1.203
<u>X</u> / <u>Xa</u>	106.68	1.194 ^d	33.5 ^d	1.201 ^e
	107.35	1.206 ^d		
<u>XI</u> / <u>XIa</u>	118.09	1.188 ^d	34.0 ^d	1.195

^aFor 2 atoms of α -D.

^bExtrapolated from other temperatures assuming $A_{\underline{H}}/A_{\underline{D}} = 1.0$.

^cSee reference 27a.

^dSee reference 27b.

^eAverage of two extrapolated values 1.195 and 1.208.

The α -effects for meso- and dl-IX and X, extrapolated to 105.28°C, compared to the α -effect for V suggest a more reactant-like transition state for IX and X than for V. This phenomenon was assumed to result from a more hindered reactant conformation for the diastereoisomers of IX and X.^{20,27b} Both systems were judged to possess comparable strain energies: E_s for phenyl is -0.38 and E_s for ethyl is -0.36.²⁸ The very similar α -effects for the diastereoisomers of IX and X supports the hindered-reactant hypothesis. The activation energies for the decomposition of meso- and dl-IX and X are similar to if not larger than the value for V.^{27b}

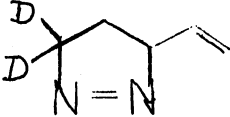
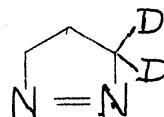
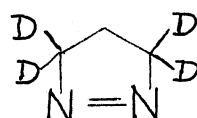
The steric and electronic effects of the methoxy substituent (in XI), which place opposite demands on the reactant- and radical-likeness of the transition state, were deemed approximately to cancel and so yield a value of k_H/k_D similar to the α -effect for V.^{27b} The α -effect for the thermal decomposition of XI was approximately 29 percent lower than the α -effect for V. The origin of this abnormal α -effect is obscure. It was suggested that the decomposition of XI might occur via a transition state in which each methoxy group was in a bisected conformation.²⁹ Such a transition State, if more reactant-like in the decomposition of V, would be consistent with the α -effect of 1.194. Since XI exhibits a larger E_a than V, the transition state for XI might be more radical-like. In passing from a reactant to the transition state the reduction in the α -H-C-N bending force constant would necessarily be greater for XI than for V. Hence an increase in one or more of the remaining force constants associated with each α -hydrogen would be required to produce an α -effect for XI of 1.194.

Crawford and coworkers³⁰ have measured secondary deuterium isotope

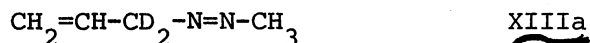
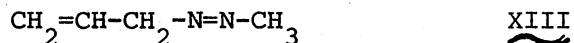
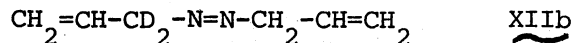
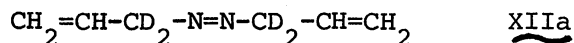
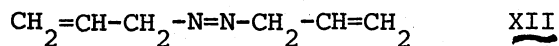
effects for the thermolysis of several 1-pyrazolines. The data for thermal decomposition of 1-pyrazolines in Table VII was argued to be indicative of simultaneous rupture of both carbon-nitrogen bonds on the basis of the magnitude of the isotope effects observed. Crawford and coworkers also investigated the thermal decomposition of 3,3'-azo-1-propene (XII) and 3-(methylazo)propene (XIII).^{30c} α -Secondary deuterium isotope effects in decomposition of XII and XIII were investigated using α -deuterated derivatives XIIa and XIIb and XIIIa, respectively.

TABLE VII

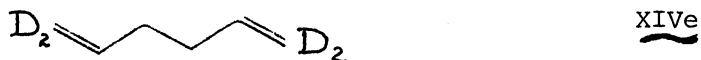
SECONDARY KINETIC ISOTOPE EFFECTS FOR α -DEUTERATED 1-PYRAZOLINES

Compound	Temperature	$k_{\text{H}}/k_{\text{D}}$ obs.
	134.5	1.21 ^a
	229.4	1.19 ^b
	229.4	1.40

^a Reference 30a.^b $k_{\text{H}}/k_{\text{D}}$ at 105°C 1.26 - reference 30b.^c $k_{\text{H}}/k_{\text{D}}$ at 105°C 1.55 - reference 30b.



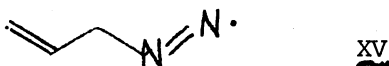
XII decomposed thermally in the vapor phase to yield greater than 99.9% 1,5-hexadiene (XIV). For the decomposition of XIIa and XII statistical scrambling of deuterium in the products occurred. The n.m.r. analysis of the 1,5-hexadienes from the decomposition of XIIb gave product distributions of 4:4:4:2:1:1 of XIV, XIVa, XIVb, XIVc, XIVd, and XIVe, respectively.



Similar n.m.r. analysis of the 1,5-hexadienes from the decomposition of XIIa yielded a 2:1:1 mixture of XIVc, XIVd and XIVe, respectively.

Examination of the recovered starting material after thermolysis of

XIIa to forty percent completion showed that the deuterium in the vinylidene position of XIV increased approximately four percent. The partial decomposition of XIIb under the same reaction conditions generated approximately two percent of XIIa, at forty percent decomposition as detected by mass spectrometry. This scrambling was attributed to either reversible addition of an allyl radical to the azo starting material or to trapping of allyl radicals by the nitrogen radical XV.³⁰



If a simultaneous rupture mechanism is operative, the α -deuterium isotope effect for XII yields a $\Delta\Delta G^\ddagger$ of 60 cal mole⁻¹ per deuterium. If a stepwise rupture mechanism is operative, the value of $\Delta\Delta G^\ddagger$ is 120 cal mole⁻¹ per deuterium. Examination of XIII/XIIIa gives a k_H/k_D ratio of 1.28 ± 0.03 at 126.0°C ($\Delta\Delta G^\ddagger = 98 \pm 9$ cal mole⁻¹ per deuterium). These data were considered comparable to values generally encountered in the thermolysis of azo compounds wherein the transition state occurs late along the reaction coordinate.³¹ The above arguments coupled with an excellent Polanyi plot observed by Al-Sader and Crawford^{30b} for symmetrical azoalkanes lead to the conclusion that in the gas phase, azo compounds fragment into only two species in the rate-determining step. This conclusion is thought by Crawford to be consistent with data from the earlier study of 1-pyrazolines.^{30a}

In a further study of the relationship between α -effects and reactant structure for thermolysis of azo compounds, 2,2,2',2'-tetramethyl-1,1'-diphenylazopropane (XVI) and 1,1',3,3,3',3'-hexaphenylazopropane (XVII) were chosen for the investigation here reported. Because of its singular importance in the interpretation of the α -effects for

structurally related compounds, the magnitude of the α -effect for the thermolysis of V was remeasured.

CHAPTER II

RESULTS AND DISCUSSION

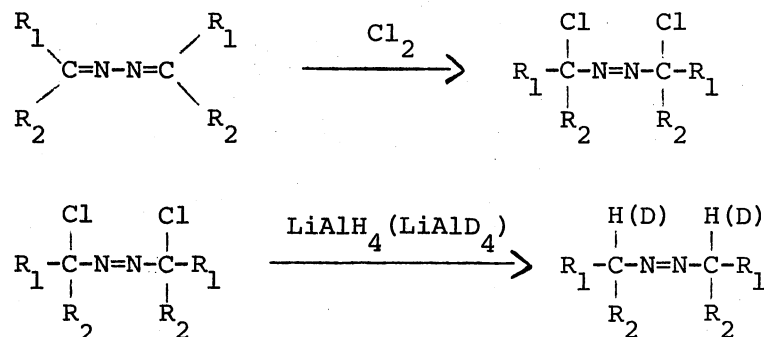
α,α,α -Trifluoroacetophenone (XVIII) was synthesized by the procedure of Dishart and Levine.³² α,α,α -Trifluoroacetophenone azine (XIX) could not be synthesized by reaction of XVIII with hydrazine (2:1 mole ratio, respectively) in ethanol. The azine was therefore prepared by reaction of α,α,α -trifluoroacetophenone hydrazone³³ with XVIII in ethanol containing a trace of benzenesulfonic acid. However, all attempts to convert XIX to the corresponding azo compound failed. Thus, an attempt was made to synthesize 2,2'-difluoro-1,1'-diphenylazoethane (XX). Because of the extreme toxicity of the reagents (sodium fluoroacetate or fluoroacetyl chloride) used in the literature synthesis³⁴ of α -fluoroacetophenone (XXI), this ketone was prepared in fifty percent yield by treating phenacyl bromide with anhydrous potassium fluoride in refluxing xylene. Although conversion of XXI to α -fluoroacetophenone azine (XXII) was facile, all attempts at conversion of XXII to XX failed. The following attempts were made to synthesize XX. Reduction of XXII with hydrogen using either five percent palladium on carbon or palladium on barium sulfate as the catalyst resulted in partial cleavage of the carbon-fluorine bond. Addition of chlorine to XXII followed by reduction with sodium borohydride gave no reaction. Addition of chlorine to XXII followed by reduction of the dichloro azo compound with lithium aluminum hydride yielded products which according to n.m.r.

analysis of the crude mixture had undergone extensive cleavage of the carbon-fluorine bond.

2,2-Dimethylpropiophenone (XXIII) was synthesized by reaction of diphenylcadmium with trimethylacetyl chloride. Acetophenone azine (XXIV), 2,2-dimethylpropiophenone azine (XXV) and β,β -diphenylpropio-phenone azine (XXVI) were prepared by refluxing two moles of ketone with one mole of hydrazine in ethanol containing a small amount of glacial acetic acid.

A new synthetic route to secondary azo compounds, Scheme XII, has been developed based upon the use of 1,1'-dichloro azo compounds¹⁰ and their known reactivity with nucleophiles.^{10d} The preparation of

SCHEME XII



1,1'-dichloro-1,1'-diphenylazoethane (XXVII) was accomplished by addition of chlorine to XXIV in methylene chloride at -70°C .^{10a} Similarly XXV was converted to 1,1'-dichloro-2,2,2',2'-tetramethyl-1,1'-diphenylazopropane (XXVIII) at 0°C . Reaction was not realized at -70°C as reported in the literature.^{10a} Reaction of XXVI with chlorine in methylene chloride at -70°C and 0°C gave a product which upon heating evolved gas. However, mass spectral analysis of the crude product

(introduced into the ion source via the direct probe) provided evidence for the presence of products containing more than two chlorines.

Grizzle³⁵ has prepared 1,1'-dichloro-1,1',3,3,3',3'-hexaphenylazopropane (XXIX) by Scheme XII. XXIX was found to produce XVII in 60 percent yield when refluxed in ether with lithium aluminum hydride for 18 hours.³⁵

Conversion of XXVII and XXVIII to V and XVI (to Va and 2,2,2',2'-tetramethyl-1,1'-diphenylazopropane-1,1'-d₂ (XVIa)) was accomplished by refluxing XXVII and XXVIII with lithium aluminum hydride (or lithium aluminum deuteride) in ether. This new technique avoids the oxidation step requiring an oxidizing agent and/or reduction products of the oxidizing agent which might cause tautomerization of the product azo compound and also allows the specific introduction of a deuterium into the alpha position of the azo compound. The isotopic enrichment is limited only by the atom percent deuterium available in lithium aluminum deuteride.

Upon pyrolysis in ethylbenzene recrystallized XVI failed to yield nitrogen quantitatively. The low yield of nitrogen was attributed to the presence of a trace amount of XXVIII. 1,1'-Dichloroazoalkanes are known to undergo thermal decomposition via C-N bond homolysis.^{10b-e} There may be some C-Cl bond cleavage which could lead to the formation of trace amounts of HCl. The trace of HCl would cause tautomerization of XVI to hydrazone.³⁶ Further purification of XVI via recrystallization, column chromatography on neutral alumina followed by recrystallization, and extraction with aqueous bicarbonate followed by recrystallization also failed to yield a sample of XVI which upon pyrolysis in ethylbenzene would give a quantitative yield of nitrogen. The pyrolysis

of XVI in ethylbenzene containing pyridine³⁶ in a 6:1 mole ratio gave 99.1 percent yield of nitrogen. This result is consistent with the above explanation for the low yield of nitrogen.

A purification technique of azo compounds synthesized via Scheme XII has been developed from the known solvolytic reactions of 1,1'-dichloroazoalkanes.^{10b} Thus, a solution of XVI in water, ether, and acetone containing silver nitrate is stirred at room temperature. The azo compound is then extracted into ether, and washed with water, a saturated solution of sodium carbonate and water, and then dried. The ether is removed under reduced pressure and the azo compound is chromatographed over silica gel and then recrystallized. All azo compounds (V, Va, XVI, XVIa) prepared via Scheme XII were purified via the above solvolytic method. The pyrolysis in ethylbenzene of V, Va, XVI and XVIa after purification gave 99.6, 100.8, 99.0 and 99.2 percent yields of nitrogen respectively, see Table VIII.

The synthesis of XVII was accomplished by reduction of XXVI in benzene with gaseous hydrogen and five percent palladium on carbon. The alpha-deuterated analog (XVIIa) was prepared in the same manner using gaseous deuterium. Two forms of XVII and XVIIa were found upon fractional recrystallization and were labeled high-melting form (HMF) and low-melting form (LMF). The two forms are distereoisomers resulting from the introduction of two chiral centers upon the reduction of XXVII. The HMF and LMF are tentatively assigned as the meso- and dl-diastereomers, respectively.²⁷

Another sample of V was prepared by reduction of XXIV in 1,4-dioxane with gaseous hydrogen and five percent palladium on carbon and labeled V-B. The alpha-deuterated analog was prepared in benzene with

TABLE VIII
PERCENT NITROGEN EVOLVED UPON PYROLYSIS OF AZO
COMPOUNDS IN ETHYLBENZENE^a

Compound	Percent N ₂
<u>V-A</u>	99.56 ^{b,c}
<u>Va-A</u>	100.84 ^{d,e}
<u>XVI</u>	98.99 ^{c,f}
<u>XVIa</u>	99.20 ^{e,f}
<u>XVII-HMF</u>	94.46 ^d
<u>XVIIa-HMF</u>	98.71 ^d
<u>XVII-LMF</u>	98.43 ^d
<u>XVIIa-LMF</u>	97.45 ^d

^a Sample prepared and pyrolyzed by D.W.M. and yields of nitrogen determined by Dr. P. L. Grizzle.

^b Average of three determinations. V prepared via Scheme VII gave 99.33 percent nitrogen.

^c Prepared by Scheme XII using lithium aluminum hydride.

^d A single determination.

^e Prepared by Scheme XII using lithium aluminum deuteride.

^f Average of two determinations.

gaseous deuterium and five percent palladium on carbon and labeled Va-B. The samples of V and Va prepared via Scheme XII were labeled V-A and Va-A, respectively.

The azo compounds to be used for kinetics were pyrolyzed and the quantity of nitrogen evolved was determined. The results tabulated in Table VIII demonstrate that the decompositions are ninety-eight to one hundred percent complete.

The mass spectra of the decomposition products of V, Va, XVI, XVIa, XVII (HMF and LMF) and XVIIa (HMF and LMF) did not show the presence of compounds resulting from rearrangement to the corresponding hydrazone in any case. Table IX tabulates the physical constants of azo compounds that were studied.

TABLE IX
PHYSICAL CONSTANTS OF AZO COMPOUNDS

Compound	M.p., °C	Absorption	
		$\lambda_{\text{max}}, \overset{\text{O}}{\text{A}}$	ϵ_{max}
<u>V</u>	71-71	3590	48.6
<u>Va</u>	71-72	3590	48.5
<u>XVI</u>	156-156.5	3690	23.4
<u>XVIa</u>	156-156.5	3690	23.3
<u>XVII-HMF</u>	147-147.5	3640	46.4
<u>XVIIa-HMF</u>	147-147.5	3640	47.0
<u>XVII-LMF</u>	121-122	3650	50.5
<u>XVIIa-LMF</u>	121-122	3650	51.0

First order kinetics were observed for the decomposition a) of V-A and V-d₂-A (Va-A) prepared by reduction of XXVII with LiAlH_4 and LiAlD_4 ,^{35b} respectively; b) of V-B and V-d₂-B (Va-B) prepared by catalytic hydrogenation and deuteration, respectively, of acetophenone azine; c) of XVI and XVIa; and d) of XVII-HMF, XVIIa-HMF, XVII-LMF and XVIIa-LMF.

The kinetics of the thermal decomposition of the azo compounds were found by observing the decrease in optical density (O.D.) due to the azo chromophore at λ_{max} as a function of time. The data were solved for the best fit to the following equation using the method of nonlinear least-squares and an I.B.M. 360/65 computer, see Appendix A.

$$y = A + Be^{-kt}$$

The initial values of A, B and k were estimated from the plot of log O.D. vs. time. The isotope effects were measured by simultaneously observing the rate of decomposition of the protiated and deuterated azo compounds in ethylbenzene.²¹ The activation parameters were calculated by a linear least-squares analysis of the variation of log k with the inverse of the absolute temperature (see Table X).^{27a} Table XI presents the observed and corrected (2 atoms of $\alpha\text{-D}$) isotope effects and the deuterium content of each deuterated compound as determined by combustion or for Va-B,^{35a} XVIIa-HMF and XVIIa-LMF by n.m.r. proton ratios from integration.²⁷ For Va-A the value for atoms of deuterium by combustion was 1.9602 ± 0.002 . For Va-B the corresponding value was 1.8099 ± 0.0027 (1.830 ± 0.106 by n.m.r.: 1.585 ± 0.016 atoms of $\alpha\text{-D}$ and 0.245 ± 0.105 atoms of $\beta\text{-D}$).^{35a} XVIa was found to contain 1.998 ± 0.003 atoms of D by combustion. XVIIa-HMF and XVIIa-LMF were found to

TABLE X

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE THERMOLYSIS
OF AZOALKANES IN ETHYLBENZENE

Compound	Temperature °C	$k \times 10^3, \text{min}^{-1}$	E_a kcal/mole	ΔS^\ddagger e.u.
<u>XVI</u>	137.84 ± 0.19	1.9889		
	150.26 ± 0.16	8.0658	37.8 ± 0.4	10.3 ± 0.9
	158.27 ± 0.20	18.5204		
<u>XVII-HMF</u>	95.97 ± 0.04	1.9480		
	106.07 ± 0.04	6.9521	34.1 ± 0.3	11.1 ± 0.9
	113.98 ± 0.05	17.0054		
	114.51 ± 0.07	18.2119		
<u>XVII-LMF</u>	95.97 ± 0.04	3.6327		
	104.91 ± 0.06	10.3778	32.0 ± 0.3	6.5 ± 0.8
	114.85 ± 0.06	30.4497		

TABLE XI
ISOTOPE EFFECTS AND DEUTERIUM CONTENT FOR AZOALKANES

Compound	$(k_{\text{H}}/k_{\text{D}})_{\text{obs.}}$	Temperature, °C	Number Deuterium/Molecule	$(k_{\text{H}}/k_{\text{D}})_{\text{corr.}}^{\text{a}}$
<u>V-A</u>	$1.1912 \pm 0.0060^{\text{b}}$	103.90 ± 0.02	$1.9602 \pm 0.002^{\text{c}}$	1.195 ± 0.006
<u>V-B</u>	$1.1590 \pm 0.0104^{\text{d}}$	103.90 ± 0.1	$1.585 \pm 0.016^{\text{ce}}$	1.198 ± 0.014
<u>XVI</u>	$1.1991 \pm 0.0047^{\text{f}}$	137.84 ± 0.19	$1.998 \pm 0.003^{\text{c}}$	1.199 ± 0.005
	$1.1722 \pm 0.0150^{\text{d}}$	150.26 ± 0.16		1.172 ± 0.015
	$1.1573 \pm 0.0076^{\text{d}}$	158.27 ± 0.20		1.158 ± 0.008
<u>XVII-HMF</u>	$1.1441 \pm 0.0061^{\text{d}}$	106.07 ± 0.04	$1.5029 \pm 0.0057^{\text{cg}}$	1.196 ± 0.008
<u>XVII-LMF</u>	$1.2086 \pm 0.0070^{\text{f}}$	104.91 ± 0.06	$1.5086 \pm 0.0076^{\text{ch}}$	1.286 ± 0.010

^a For two deuteriums per molecule.

^b Six of six determinations.

^c By combustion analysis.

^d Five of five determinations.

^e n.m.r. analysis yielded 1.830 ± 0.106 atom deuterium per molecule: 1.585 ± 0.016 atoms of $\alpha\text{-D}$ and 0.245 ± 0.105 atoms of $\beta\text{-D}$.

^f Four of four determinations.

^g n.m.r. analysis yielded 1.4912 ± 0.0637 atoms of $\alpha\text{-D}$, see Appendix C.

^h n.m.r. analysis yielded 1.4878 ± 0.0540 atoms of $\alpha\text{-D}$, 0.0224 ± 0.1876 atoms of $\beta\text{-D}$ and 0.1158 ± 0.1076 atoms of $\gamma\text{-D}$, see Appendix C.

contain 1.5029 ± 0.0057 and 1.5086 ± 0.0076 atoms of \underline{D} , respectively, by combustion. XVIIa-HMF was found to contain 1.4912 ± 0.0637 atoms of $\alpha\text{-}\underline{D}$ by integration following repetitive scanning of the n.m.r. spectrum. The deuterium content by integration differs by less than one percent from that shown by combustion analysis of XVIIa-HMF. Integration after repetitive scanning of the n.m.r. spectrum of XVIIa-LMF yielded 1.5484 ± 0.0242 atoms of $\alpha\text{-}\underline{D}$, 0.0621 ± 0.0980 atoms of $\beta\text{-}\underline{D}$ and 0.1232 ± 0.3646 atoms of $\gamma\text{-}\underline{D}$.

The corrected isotope effects for Va-B of 1.198 ± 0.014 is considered to be in very good agreement with the corrected value of 1.195 ± 0.006 for Va-A at 103.90 ± 0.1 and $103.90 \pm 0.02^\circ\text{C}$, respectively. In measuring $k_{\underline{H}}/k_{\underline{D}}$ for V-B/Va-B difficulties were encountered in achieving long-term temperature stability.

The α -deuterium isotope effect for the decomposition of V is a) 1.195 rather than 1.27^{21} and comparable in magnitude to the α -deuterium isotope effects obtained for IX, X and XI.^{27,37} To consider the implications of this result, the α -effects for the decomposition of V, IX, X and XI have been extrapolated to 105.28°C on the assumption that $A_{\underline{H}}/A_{\underline{D}}$ equals one (Table XII).³⁸ The previous conclusion that the decomposition mechanism changes from unsymmetrical one-step cleavage to two-step cleavage in the series V, IV and VIII is consistent with an α -effect of 1.195 for V. Consideration of the data for VII, IV and V in terms of the mechanism presented in Scheme XIII, XIV and XV establishes the validity of this conclusion.

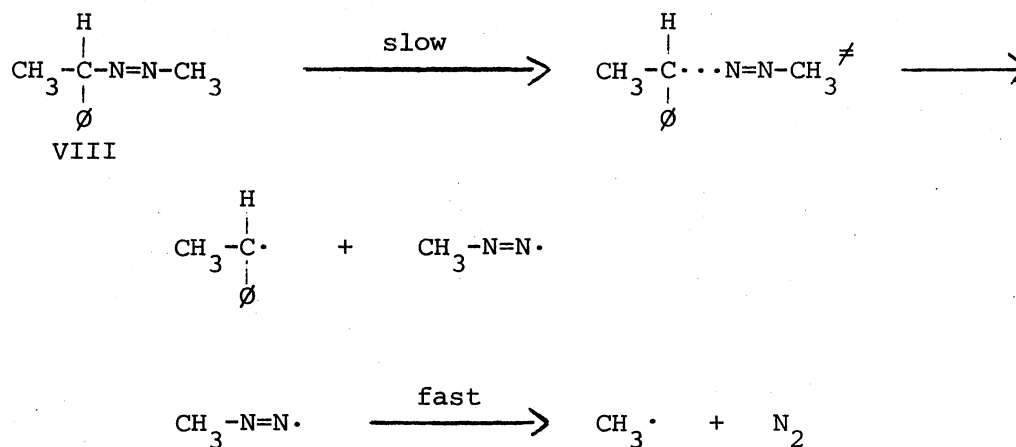
TABLE XII

 α -SECONDARY DEUTERIUM ISOTOPE EFFECTS FOR THE DECOMPOSITION OF AZOALKANES

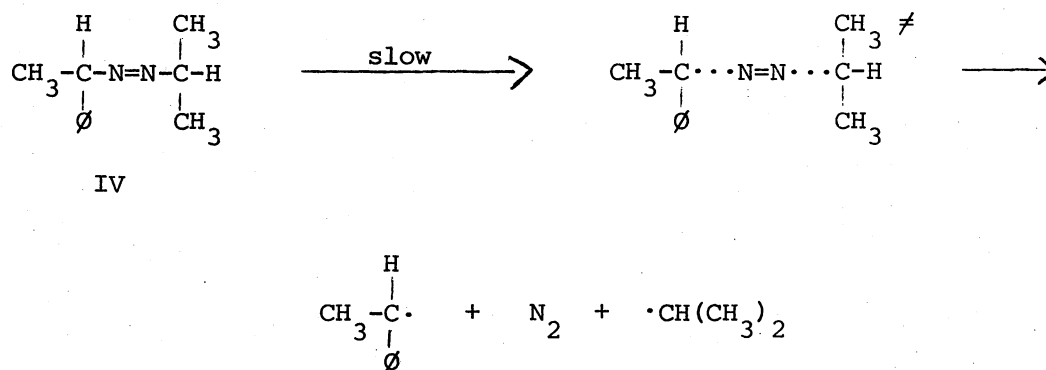
Compound	$(k_{\text{H}}/k_{\text{D}})_{\text{exp}}^{\text{a}}$	Temp., °C	Position	$k_{\text{H}}/k_{\text{D}}^{\text{b}}$ 105.28°	$k_{\text{H}}/k_{\text{D}}$ per D ^c 105.28°
V-A	1.195 ± 0.006	103.90	Benzyl	1.194	1.093
IV	1.148 ± 0.012 ^d	143.20	Benzyl	1.164	1.164
	1.036 ± 0.007 ^d	143.20	Propyl	1.040	1.040
VII	1.13 ± 0.01 ^e	161.00	Benzyl	1.151	1.151
	0.97 ± 0.01 ^e	161.00	Methyl	0.966	0.989
IX	1.224 ± 0.006 ^f	106.47	Benzyl	1.225	1.107
	1.202 ± 0.006 ^f	106.47	Benzyl	1.203	1.097
X	1.194 ± 0.008 ^g	106.68	Benzyl	1.201 ^h	1.096
	1.206 ± 0.014 ^g	107.35	Benzyl		
XI	1.188 ± 0.004 ^g	118.09	Benzyl	1.195	1.093

^aCorrected to max atoms of D at the indicated position.^bFor maximum number of atoms of D at the indicated position.^cCalculated by taking the n^{-1} root of the value in column 5 where n is the number of atoms of D at a specified position.^dSee Ref. 22; ^eSee Ref. 23; ^fSee Ref. 27a; ^gSee Ref. 27b.^hAverage of two extrapolated values, 1.195 and 1.208.

SCHEME XIII

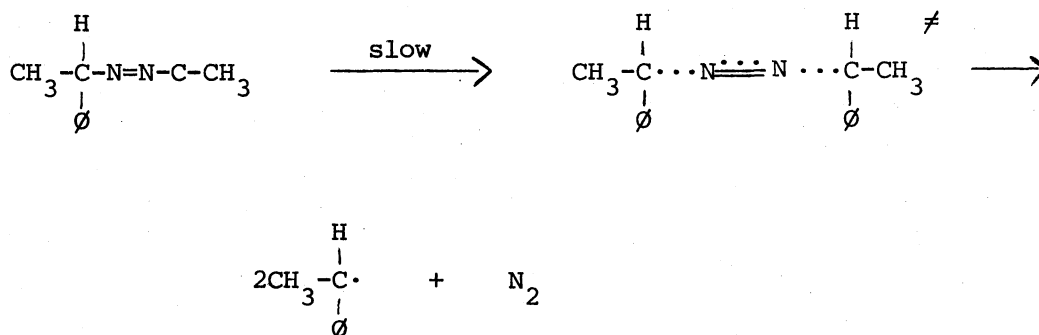


SCHEME XIV



"Exact" calculations in model chemical systems have shown that the magnitude of the α -effect is dependent upon the change in the hydrogen-carbon-leaving group bending force constant (HCN), i.e., $f_{\text{HCN}} - f_{\text{HCN}}^\neq$, in passing from the reactant to the transition state.^{18a-c,39} Thus, the α -effect reflects the extent of bond rupture between the α -carbon and the leaving group at the saddle point. The α -effect for VIII at the benzylic position ($k_{\text{H}}/k_{\text{D}} = 1.13$ at 161^o C, see Table IV) indicates rupture of the 1-phenylethyl carbon-nitrogen bond.²³ The β -effect for

SCHEME XV



VIII/VIIIb of 0.97 suggests a slightly stronger CH_3 -N bond in the transition state than in the reactant state.²³ The "exact" analysis of the isotope effects for VIII yields a transition-state model for which the force constants are consistent with the qualitative interpretation of the experimental data.^{20,25a} For the decomposition of IV at 143.20°C the α -effects of 1.15 for IVa and 1.036 for IVb show that the homolysis of both C-N bonds is occurring in the rate-controlling step.²² The "exact" analysis of both α -secondary deuterium and of the primary nitrogen isotope effects leads to a set of transition-state force constants consistent with Scheme XIV. The decrease in the energy and entropy of activation in going from VIII ($E_a = 38.6$ kcal/mole, $\Delta S^\ddagger = 14.0$ eu)³ to IV ($E_a = 36.5$ kcal/mole, $\Delta S^\ddagger = 9.3$ eu)¹⁴ is consistent with some rupture of and restricted rotation about the $(\text{CH}_3)_2\text{CH-N}$ bond in the activated complex.^{23,40} The results are both consistent with an unsymmetrical one-step mechanism for pyrolysis of IV.

The results for IV and VIII are not consistent with a two-step mechanism for V. The α -effect for VIII at the benzylic position pre-

dicts a $k_{\text{H}}/k_{\text{D}}$ of 1.15-1.16 for the thermal decomposition of V via a two-step mechanism at 105.28°C. The α -effect for two-step and one-step thermolysis of V/Va is difficult to predict, because the activation energy for V of 32.6 kcal/mole suggests a more reactant-like transition state and therefore, a smaller change in f_{HCN} per C-N bond rupture for V than for IV or VIII. For the thermolysis via a one-step mechanism the $k_{\text{H}}/k_{\text{D}}$ for V/Va at 105.28°C should be larger than the extrapolated benzylic α -effects for IV and VIII.⁴¹ The experimental value ($k_{\text{H}}/k_{\text{D}} = 1.195$) is greater than the values obtained upon extrapolating the observed benzylic effect IV and VIII to 105.28°C (see Table XII). Therefore, the α -effect for the thermolysis is qualitatively consistent with a one-step mechanism. "Exact" analysis²⁶ of both the α -deuterium and primary nitrogen isotope effects for the thermolysis of V results in a model (Vmb) for the activated complex which is inconsistent with the experimental value of 1.195. The magnitude of the decrease in the f_{HCN} in passing from the reactant state to the transition state for the decomposition of V must be less than the decrease required to produce the value of 1.27. Seltzer and Mylonakis²⁶ have described two transition state models Vma and Vmb which produce an α -effect of 1.27; in both models $f_{\text{HCN}}^{\ddagger}$, $f_{\text{CCN}}^{\ddagger}$, $f_{\text{C}_6\text{H}_5\text{CN}}^{\ddagger}$ and $f_{\text{CNN}}^{\ddagger}$ are forty percent of the corresponding reactant state values. Vmb gives a better fit to the nitrogen isotope effect than Vma (see Table V). Vmb differs from Vma in the magnitude of the C-N stretching force constant and the interaction force constant $f_{\text{int}}^{\ddagger}$.⁴² Seltzer and Hamilton⁴² have described another transition state model (Vmc) which appears to be like Vma except that all the bending force constants associated with the leaving group are about fifty-five percent rather than forty percent of the reactant state

values. \underline{V}_{mc} predicts an α -effect of 1.193 at 100°C. It appears reasonable to conclude that \underline{V}_{mb} , in which f_{-HCN}^\ddagger , f_{-CCN}^\ddagger , $f_{-C_6H_5CN}^\ddagger$ and f_{-CNN}^\ddagger are about fifty-five percent rather than forty percent of the reactant State values, still constitutes a reasonable description of the bonding in the transition state for the thermal decomposition of \underline{V} . Other kinetic evidence which favors a concerted mechanism is as follows. Both E_a and ΔS^\ddagger (32.6 kcal/mole and 7 e.u., respectively)¹³ for \underline{V} are in harmony with an activated complex involving delocalization of two incipient p -electrons over two aromatic π -systems accompanied by restricted rotation of the phenyl groups. The absence of a viscosity dependence on the rate of thermolysis of structurally related \underline{VI} , 2,2'-diphenylazo-2-propane, also constitutes indirect supporting evidence of a one-step mechanism.¹⁵ Similarly the α -effects and activation parameters for both diastereomers of \underline{IX} , \underline{X} and \underline{XI} are entirely consistent with a concerted mechanism for thermolysis of these compounds.²⁷

The magnitude of k_{-H}/k_{-D} reflects the reaction in f_{-HCN}^\ddagger upon passing from the reactant state to the transition state.^{18c,26} If the force constants associated with the α -CH bond in the reactant states are transferable⁴³ within a few percent,^{27b} the α -effects for $\underline{dl-IX}$, \underline{X} and \underline{XI} compared to \underline{V} suggest that substitution of phenyl, ethyl and methoxy for α -hydrogen in \underline{V} does not seriously perturb that part of the potential energy hypersurface involving motion of the α -hydrogen. If such perturbations do occur they must be compensated by factors such as coupling of vibronic motions and/or curvature in the barrier. The α -effects then indicate only a small substituent effect, if any, on the reactant-like: product-like character of the transition state. The α -deuterium and nitrogen isotope effects for $\underline{meso-IX}$ ($k_{-H}/k_{-D} = 1.224$ at

106.47°C and $k_{-14}/k_{-15} = 1.0158$ at 106.42°C)⁴⁴ are respectively larger and smaller than the values for V ($k_{-H}/k_{-D} = 1.194$ at 105.28°C and $k_{-14}/k_{-15} = 1.0229$ at 105.02°C).²⁶ Previously the α -deuterium and primary nitrogen isotope effects were interpreted as favoring a more reactant-like transition state for meso-IX than for V.²⁹ If in passing from the reactant state to the transition state changes in bending force constants are correlated with changes in stretching force constants,²⁶ and if the consequences²⁶ of this correlation of k_{-H}/k_{-D} and k_{-14}/k_{-15} are considered, the isotope effects for meso-IX compared to V are consistent with smaller values of f_{-HCN}^\ddagger and f_{-CN}^\ddagger and an increased value for f_{-NN}^\ddagger for the former. Thus, both the deuterium and the nitrogen isotope effects are qualitatively reconcilable with a more radical-like transition state for meso-IX than for V.

A linear least-squares fit of $\ln k_{-H}/k_{-D}$ versus $1/T^\circ K$ of the α -effects for the thermal decomposition of XVI (1.1991 at 137.84°C, 1.1722 at 150.26°C and 1.1573 at 158.27°C) yields a A_{-H}/A_{-D} value of 0.75 ± 0.08 per D. This ratio of pre-exponential factors per D is not in good agreement with those obtained per D from the unimolecular decomposition of the t-cumyloxy-d₃ radical⁴⁵ (0.98) and from "exactly" calculated isotope effects for the decomposition of 1,1'-diphenylazoethane-1,1'-d₂ (Va) by Seltzer and Hamilton⁴² (0.96 for transition-state model Vma). The scatter in the α -effects are demonstrated in the standard deviation of the A_{-H}/A_{-D} value and in the span and overlap of the α -effects measured at each temperature, see Appendix B. This scatter will not allow an accurate extrapolation of the α -effect for XVI to 103.9°C to compare with the α -effect of V. The α -effects for XVI can only be bracketed within limits of the scatter, i.e., 1.205 to 1.149 per 2-D,

see Appendix B.

Table XIII presents the relative rate constants at 103.90°C and the activation parameters for the thermolysis of V, VIII and XVI. It should be noted that the rate of thermolysis of V at 103.90°C is about 140 times higher than for XVI. This could be interpreted as indicating the absence of significant intramolecular repulsive interactions in the reactant state. However, inspection of molecular models of XVI indicates potential interaction between the methyl groups of the t-butyl and ortho-hydrogens of the ring. Furthermore Severn and Kosower have postulated that the difference in λ_{\max} of the $n-\pi^*$ transitions for a given class of azo compounds reflects differences in nonbonded interaction in their ground state.⁴⁶ XVI ($\lambda_{\max} = 369$ nm) should possess 2.2 kcal/mole of strain energy compared to V ($\lambda_{\max} = 359$ nm). Therefore, XVI should decompose faster than V. The rate data for XVI compared to V indicates that reactant-state nonbonded interactions are not the only factors controlling the reaction energetics for the thermolysis of XVI. Steric inhibition of resonance in the transition state is one possible factor. Steric inhibition of resonance in the transition state has been advanced to explain the decrease in the rate of solvolysis of 1-phenyl-2,2-dimethylpropyl chloride compared to 1-phenylethyl chloride.⁴⁷

The decrease in ΔS^\ddagger in passing from VIII to V was interpreted in terms of increased restricted rotation in the transition state of the forms resulting from homolysis of both C-N bonds.²³ It should be noted that the E_a for XVI is more similar to the ones observed for the decomposition of secondary azoalkanes than secondary azo compounds containing one phenyl group per α -carbon. The similarities of the energy of

TABLE XIII
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE
THERMOLYSIS OF AZOALKANES

Compound	Temp. °C	$k \times 10^3 \text{ min}^{-1}$	Relative rate at 103.9°C	E_a kcal/mole	ΔS^\ddagger e.u.
<u>V</u>	103.90	4.50	141	32.6 ^a	7.0 ^a
<u>XVI</u>	158.27	18.52	1.00 ^b	37.8	10.3
<u>VIII</u>	161.00	6.97 ^c	1.21 ^b	38.6 ^c	14.0 ^c

^aSee reference 14.

^bExtrapolated from data at other temperatures.

^cSee reference 23.

activations and entropies of activation for the thermolysis of XVI and VIII could indicate a similar decomposition mechanism. The slight reduction of the E_a for the thermolysis of XVI compared to VII results from nonbonded interactions in the reactant state. The ΔS^\ddagger for XVI is somewhat less than ΔS^\ddagger for VIII since the role of thermolysis of XVI is favored by a statistical factor of two. These data will not lend themselves to any other elucidation of mechanism of the thermolysis of XVI.

Grizzle^{35a} has remeasured the α -effects for XVI (1.177 per 2-D extrapolated to 103.90°C) and concluded on the basis of the α -effect, viscosity dependence of the rate of decomposition and the α -effect for the thermolysis of (2,2'-dimethyl-1-phenylpropyl-1-d)azomethane (1.261 per D at 103.90°C) that the mechanism for the thermolysis of XVI involves two steps.

The activation energies and entropies of activation for the decomposition of XVII-HMF and XVII-LMF are 34.1 kcal/mole and 11.1 e.u. and 32 kcal/mole and 6.5 e.u., respectively. The activation energies for XVII-HMF and XVII-LMF are consistent with the two-bond rupture mechanism for their decomposition,^{7,13,14,27} see Table X. The entropy of activation for XVII-HMF indicates a greater amount of disorder in passing from the reactant state to the transition state for this compound than for V.⁷ The entropy of activation for XVII-LMF is similar to the value for decomposing V.⁷ The α -effect for the decomposition of XVII-HMF of 1.196 at 106.07°C is quite normal compared to the value of 1.194 at 105.28°C for V. The transition state for decomposition of XVII-HMF must be similar to transition state for decomposing V. The α -effect for the decomposition of XVII-LMF of 1.286 at 104.91°C is not consistent with the value of 1.194 at 105.28°C for the decomposition of V. The large

value of the α -effect for XVII-LMF compared to the value for V indicates a more radical-like transition state. This increase in the α -effect requires a large reduction in $f_{\text{-HCN}}$ for XVII-LMF upon passing from the reactant state to the transition state. The α -effects XVII-HMF and XVII-LMF should only be considered as upper limits because of the doubts imposed by the deuterium analysis.⁴¹ The XVII compound(s) should be reinvestigated to determine the correctness of the activation parameters and isotope effects now that a new method of synthesis of XVII will allow quantitative incorporation of deuterium into the α -position.³⁵

CHAPTER III

EXPERIMENTAL

Preparation of α,α,α -Trifluoroacetophenone

(XVIII)

Trifluoroacetic acid (60 grams, 0.527 moles) dissolved in 100 ml of anhydrous ether was added dropwise to a 900 ml ethereal phenylmagnesium bromide (1.5 moles) solution in a three-neck, three-liter round bottom flask. The reaction was cooled with an ice bath during addition of trifluoroacetic acid to prevent vigorous reflux of ether. The reaction mixture was then refluxed for three and a half hours, cooled and then hydrolyzed with 600 ml of ten percent hydrochloric acid. The aqueous phase was separated from the ether phase and extracted with 500 ml portions of ether. The combined ether layers were washed with a saturated solution of sodium bicarbonate and then water, dried over anhydrous magnesium sulfate, filtered, and freed of ether under reduced pressure. Distillation of the crude product yielded fifty-five grams (60%) of XVI, b.p. $87-89^{\circ}\text{C}$ at 85 mm. (lit. b.p. 152°C at 730 mm).³²

Preparation of α,α,α -Trifluoroacetophenone

Hydrazone

Thirty grams of α,α,α -trifluoroacetophenone (0.172 moles), 545 ml of water, 36.6 grams of hydrazine dihydrochloride (0.349 moles), 67.2

grams of sodium acetate (0.820 moles) and enough ethanol (700 ml) to make the mixture homogeneous were stirred in a three-liter Erlenmeyer flask for six and a half days at room temperature. The ethanol was removed by distillation at aspirator pressure and the remaining aqueous mixture was extracted twice with 300-ml portions of ether. The combined ether extracts were washed with a saturated solution of sodium carbonate and water, dried over anhydrous magnesium sulfate, filtered and freed of ether under reduced pressure. Distillation of the crude products yielded 15.8 grams (49%) of α,α,α -trifluoroacetophenone hydrazone; b.p. 115-120°C at 13 mm (lit. b.p. 111-120°C at 22 mm).³³

Preparation of α,α,α -Trifluoroacetophenone

Azine (XIX)

α,α,α -Trifluoroacetophenone (20 grams, 0.115 moles) and crude α,α,α -trifluoroacetophenone hydrazone (32 grams, 0.172 moles) were refluxed for three hours in 100 ml. of benzene containing 0.2 grams of benzenesulfonic acid in a round-bottom flask fitted with a Dean-Stark trap. After removal of benzene under reduced pressure the crude product was separated from tars by bulb-to-bulb distillation at 0.5 mm. Recrystallization of the material from methanol yielded 19.9 g. (34%) of α,α,α -trifluoroacetophenone azine; m.p. 56-57°C, mass spectrum \underline{M}^+ at $\underline{m/e}$ 344.072 (calculated for $C_{16}H_{10}N_2F_6$, 344.074).

Preparation of α -Bromoacetophenone

A solution of acetophenone (200 grams, 1.67 moles) in 50 ml. of ether (anhydrous) was placed in a three-necked flask fitted with a separatory funnel, mechanical stirrer and reflux condenser. The solu-

tion was kept cold in an ice bath as aluminum chloride (2.0 grams) was added and bromine (223 grams, 1.67 moles) was added slowly from the separatory funnel with stirring. Complete reaction was taken to be the persistent of a reddish color, indicating the presence of unreacted bromine.

The ether and hydrogen bromide were removed under reduced pressure. The solid α -bromoacetophenone was washed with 40 ml. of water and 40 ml. of petroleum ether. The crystals were filtered out and further washed with a mixture of 40 ml. of water and 40 ml. of petroleum ether three times. The crude α -bromoacetophenone recrystallized from methanol comprised 179 grams (54%); m.p. $49-50^{\circ}\text{C}$, (lit. $49-51^{\circ}\text{C}$).⁴⁸

Preparation of α -Fluoroacetophenone (XXI)

Anhydrous potassium fluoride (233 grams, 4.01 moles) was added to a five-liter round-bottom flask containing α -bromoacetophenone (400 grams, 2.01 moles) dissolved in one liter of m-xylene. The reaction mixture was refluxed for two weeks. The excess potassium bromide and potassium fluoride are removed by filtration and m-xylene was then removed by distillation at atmospheric pressure. Water (750 ml.) was added and the mixture was extracted three times with 750-ml. portions of ether. The combined ether extracts were washed three times with 200-ml. portions of water, dried over anhydrous magnesium sulfate, filtered and freed of ether under reduced pressure. Distillation of the crude product (b.p. $151-152^{\circ}\text{C}$ at 100 mm.) yielded 171 grams (62%) of XXI; lit. b.p. $90-91^{\circ}\text{C}$ at 12 mm.⁴⁹; nmr (neat oil) δ 5.52 (d, 2H), 7.60 (m, 5H).

Preparation of α -Fluoroacetophenone Azine (XXII)

Hydrazine (1.3 grams, 0.04 moles) dissolved in 10 ml. of absolute ethanol was added slowly to 11 grams of α -fluoroacetophenone (0.08 moles) in 15 ml. of absolute ethanol previously cooled to 0°C with an ice bath. The reaction mixture was stirred for three hours at 0°C and the azine was filtered out. Recrystallization twice from ethanol gave 5 grams (46.3%) yield of α -fluoroacetophenone azine; m.p. 71-71°C, mass spectrum exhibited \underline{M}^+ at m/e 272.113 (calculated for $C_{16}H_{14}N_2F_2$, 272.112); nmr (CCl_4) δ 5.55 (d, 4H), 7.55 (m, 10H).

Preparation of 2,2-Dimethylpropiophenone (XXIII)

Dry cadmium chloride (384 grams, 2.09 moles) was added to 1.34 liters of a three-molar ether solution of phenylmagnesium bromide (4.02 moles, from Arapaho Chemical) in a three-neck five-liter round-bottom flask cooled with an ice bath. Ether was distilled and benzene added until the boiling point of the solvent reached 78°C. The volume was brought to approximately two liters with benzene. The solution was cooled with an ice bath and 2,2-dimethylpropanoyl chloride (370 grams, 3.07 moles, from Aldrich Chemical Company) in 400 ml. of benzene was added over a two-hour period. The reaction mixture was stirred at room temperature for three and a half hours and let stand for thirteen hours. The reaction mixture was poured on to ice and 50 percent aqueous sulfuric acid (1 liter) was then added to dissolve the resulting solid. The hydrolyzed reaction mixture was extracted twice with two-liter portions of ether. The combined ether extracts were washed with 10 percent aqueous sodium hydroxide, water, dried over anhydrous magnesium sulfate and filtered and the ether removed by distillation at atmospheric

pressure. The crude product was distilled yielding 469.7 grams (95%) of XXIII; b.p. 90-93°C at 6.5 mm. (lit. 80-84°C at 3 mm.).⁵⁰

Preparation of 2,2-Dimethylpropiophenone

Azine (XXV)

Pivalophenone (11 grams, 0.0678 moles) and 95 percent hydrazine (1.1 grams, 0.0327 moles) in 10 ml. of absolute ethanol containing 10 drops of acetic acid was refluxed for 84 hours. The ethanol was removed under reduced pressure. The resulting solid was taken up in ether and washed with a saturated aqueous solution of sodium bicarbonate and then with water, dried, filtered and freed of ether under reduced pressure. Recrystallization of the crude product twice from methanol yielded 8 grams (76.2%) of XXV; m.p. 80.5-81.5°C, lit. m.p. 79°C;^{10a} mass spectrum, M^+ at m/e 320.229 (calculated for $C_{42}H_{36}N_2$, 320.225); nmr (CCl_4) δ 1.09 (s, 18H), 7.06 (m, 10H).

Preparation of 1,1'-Dichloro-2,2,2',2'-Tetra-

methyl-1,1'-Diphenylazopropane (XXVIII)

Chlorine gas was added in the dark for seven hours to a solution of 10 grams (0.031 moles) of pivalophenone azine in 150 ml. of methylene chloride with the temperature maintained between 0°C and 10°C. The solution was stirred for one additional hour and then the excess chlorine and methylene chloride were removed under reduced pressure in the dark. The crude product was recrystallized from hexane yielding 11 grams (90 percent) of XXVIII; m.p. 121.5-122.5°C with gas evolution (lit. m.p. 122°C);^{10a} nmr (CCl_4) δ 1.20 (s, 18H). 7.20 (m, 10H).

Preparation of 2,2,2',2'-Tetramethyl-1,1'-Di-
phenylazopropane (XVI)

Ten grams of 1,1'-dichloro-2,2,2',2'-tetramethyl-1,1'-diphenylazopropane (0.026 moles) dissolved in 110 ml. of anhydrous ether was added at 0°C to 1.2 grams (0.32 moles) of lithium aluminum hydride suspended in 40 ml. of anhydrous ether. The reaction mixture was stirred for six hours. The mixture was cooled with an ice bath and hydrolyzed with a saturated solution of sodium potassium tartrate. The aqueous phase was separated from the ether phase and the aqueous phase was extracted twice with 300-ml. portions of ether. The combined ether extracts were washed three times with 200-ml. portions of water, dried over anhydrous magnesium sulfate, filtered and freed of ether under reduced pressure. Recrystallization of the crude product twice from methanol yielded a product with a melting point of 155.5-156.6°C. XVI was further purified by stirring XVI with silver nitrate (6 grams, 0.035 moles) in water, ether and acetone (2:4:5, ratio) in the dark for twenty hours. The ether and acetone were removed under reduced pressure and the aqueous residue was extracted three times with ether. The combined ether extracts were washed three times with water, three times with a saturated solution of sodium bicarbonate, and then water again, dried over anhydrous magnesium sulfate, filtered and freed of ether under reduced pressure. The product was recrystallized twice from hexane to yield 5.5 grams (53%) of XVI; m.p. 156-156.5°C; nmr (CCl_4) δ 1.00 (s, 18H), 3.11 (s, 2H), 7.02 (s, 10H).

Combustion analysis: calculated for $\text{C}_{22}\text{H}_{30}\text{N}_2$: C, 81.94; H, 9.38; N, 8.69. Found C, 81.81; H, 9.07; N, 9.06.

Preparation of 2,2,2',2'-Tetramethyl-1,1'-di-
phenylazopropane-1,1'-d₂ (XVIa)

Fifteen grams of 1,1'-dichloro-2,2,2',2'-tetramethyl-1,1'-diphenylazopropane (0.038 moles) was treated with 1.5 grams (0.036 moles) of lithium aluminum deuteride in the above manner. Purification of the crude product was accomplished by the same method used for XVI, yielding 6 grams (49%) of XVIa; m.p. 156-156.5° C.

Preparation of Acetophenone Azine (XXIV)

A solution of acetophenone (50 grams, 0.415 moles) and 95 percent hydrazine (7.0 grams, 0.208 moles) in 84 ml. of absolute ethanol containing 10 drops of glacial acetic acid was refluxed for ten hours. The reaction mixture was taken up in ether and the extract washed with saturated sodium bicarbonate solution and water, dried, filtered and freed from ether under reduced pressure. The crude azine was recrystallized several times from ethanol and once from hexane; m.p. 120.5-121° C (lit 124° C).^{7,14,21}

Preparation of 1,1-Dichloro-1,1'-diphenyl-
azoethane (XXVII)

Liquid chlorine (15 ml) was added to acetophenone azine in 200 ml. of methylene chloride at -70° C. The reaction mixture was stirred three hours in the dark at -70° C. The excess chlorine and methylene chloride were removed under reduced pressure in the dark yielding a light yellow solid. Recrystallization from ether yielded 20 grams (77%) of XXVII m.p. 109.5-110° C with gas evolution (lit. m.p. 110° C).¹⁰

Preparation of 1,1'-Diphenylazoethane (V)

Method a

Twelve grams of 1,1'-dichloro-1,1'-diphenylazoethane (0.39 moles) dissolved in 110 ml. of anhydrous ether was added at 0°C to a slurry of lithium aluminum hydride (3.0 grams, 0.079 moles) in 40 ml. of anhydrous ether and the resulting mixture was refluxed for six hours. The cooled reaction mixture was hydrolyzed with a saturated solution of sodium potassium tartrate. The aqueous phase was separated from the ether phase and extracted twice with 300-ml. portions of ether. The combined ether phases were washed three times with 200-ml. portions of water, dried over anhydrous magnesium sulfate, filtered and freed of ether under reduced pressure. Six grams of the resulting solid was stirred with silver nitrate (6 grams, 0.035 moles) in water, acetone and ether (200 ml, 500 ml, and 400 ml respectively) for twenty hours. The acetone and ether were removed under reduced pressure and the aqueous residue was extracted three times with 200-ml. portions of ether. The combined ether extracts were washed three times with water, three times with a saturated solution of sodium bicarbonate, and then water again, dried over anhydrous magnesium sulfate, filtered and freed of ether under reduced pressure. The product was recrystallized twice from methanol and once from hexane yielding 2 grams (21.5%) of V; m.p. 71-72°C, (lit. m.p. 72-73°C).^{7,22}

Method b

Five percent palladium-on-carbon (3 grams) suspended in 85 ml. of 1,4-dioxane which was distilled under argon from lithium aluminum

hydride directly into the hydrogenation flask was equilibrated with hydrogen gas. Acetophenone azine (15 grams, 0.064 moles) was added and reduced at atmospheric pressure. Six hours was required for the uptake of the two moles of hydrogen gas per mole of azine. The reaction mixture was filtered through a fine-grade sintered-glass funnel and the dioxane was removed under reduced pressure. The product (the colorless liquid hydrazine) was dissolved in 250 ml. of benzene and oxidized, with continuous stirring, by addition of yellow mercuric oxide in 20-gram portions until no change in the added mercuric oxide was observed (60 grams used over a two hour period). The mixture was filtered through three layers of filter paper (No. 1) and the benzene removed under reduced pressure. The crude product was repetitively recrystallized from ethanol and once from hexane and then dried under vacuum; m.p. 71-75.5°C.^{7,22}

Preparation of 1,1'-Diphenylazoethane-1,1'-d₂ (Va)

Method a

Acetophenone azine (10 grams, 0.07 moles) was converted to Va by the procedure described for V using one gram (0.024 moles) of lithium aluminum deuteride. Va was purified by the same procedure used for V. Recrystallization twice from methanol and once from hexane yielded 2 grams (21%) of Va; m.p. 71-71°C, (lit. 72-73°C).²²

Method b

Five percent palladium-on-carbon (3 grams) suspended in 150 ml. of purified benzene (distilled under argon from sodium metal directly into

the hydrogenation flask) was equilibrated with deuterium gas. Acetophenone azine (11 grams, 0.047 moles) was reduced at atmospheric pressure. Four hours were required for the uptake of the two moles of deuterium gas (2.486 liters) per mole of azine. The reaction mixture was filtered through a fine-grade sintered-glass funnel. The volume of the filtrate (colorless hydrazine in benzene) was increased to approximately 200 ml. and the hydrazine was oxidized, with continuous stirring, by addition of yellow mercuric oxide in 20-gram portions until no change in the added mercuric oxide was observed (40 grams used over a twelve-hour period). The mixture was filtered through three layers of filter paper (No. 1) and the benzene removed under reduced pressure. The crude product was recrystallized twice from hexane and then dried under vacuum; m.p. 71-72°C, (lit. m.p. 71-72°C).²²

Preparation of β,β -Diphenylpropiophenone

Azine (XXVI)

β,β -Diphenylpropiophenone (64 grams, 0.224 moles) and 3.77 grams (0.112 moles) of 95 percent hydrazine were refluxed for thirty-six hours in ethanol (180 ml.) containing 20 drops of glacial acetic acid. The reaction mixture was cooled and the crude product collected in a Buchner funnel. The azine was triturated three times with a saturated sodium bicarbonate solution and three times with distilled water to remove any traces of acid. Recrystallization of the crude product three times from benzene-methanol (50:50) yielded 54.8 grams (86.4%) of XXVI; m.p. 137.5-138°C; mass spectrum \underline{M}^+ at $\underline{m/e}$ 568.288 (calculated for $C_{42}H_{36}N_2$, 568.288); nmr δ 3.33 (d, 4H), 4.45 (t, 2H), 6.92-7.38 (m, 30H).

Preparation of 1,1',3,3,3',3'-Hexaphenylazo-1-
propane (XVII)

Five percent palladium-on-carbon (4 grams) suspended in 170 ml. of benzene (purified) was equilibrated with hydrogen gas and β,β -diphenylpropionophenone azine (12.0 grams, 0.021 moles) was added and reduced at room temperature and atmospheric pressure. Twelve hours were required for the uptake of 0.042 moles of hydrogen gas. The reaction mixture was filtered through a fine-grade sintered-glass funnel under reduced pressure. The resulting colorless solution was diluted to 250 ml. with benzene and oxidized with yellow mercuric oxide (30 grams) by stirring for fifty hours at room temperature. The suspension was filtered through three layers of filter paper (No. 42) and the benzene was removed under reduced pressure. Recrystallization of the resulting oil from 50 percent acetone and methanol at 0°C yielded the high-melting form (HMF) of product. Recrystallization of the mother liquor from 10 percent acetone in methanol in the freezer over night yielded the low-melting form (LMF). Further purification was accomplished by recrystallization of HMF from 50 percent acetone and methanol (m.p. 147-147.5°C) and of LMF from 10 percent acetone and methanol (m.p. 121-122°C).

Combustion analysis: calculated for $C_{42}H_{38}N_2$: C, 88.37; H, 6.71; N, 4.91. Found C, 87.94; H, 6.60; N, 5.38 for HMF and C, 88.14; H, 6.48; N, 5.31 for LMF.

Preparation of 1,1',3,3,3',3'-Hexaphenylazo-1-
propane-1,1'-d₂ (XVIIa)

Five percent palladium-on-carbon (3 grams) suspended in 125 ml. of purified benzene (distilled under argon from sodium metal directly into

the hydrogenation flask) was equilibrated with deuterium gas. β,β -Diphenylpropiophenone azine (13.3 grams, 0.023 moles) was reduced at room temperature and atmospheric pressure. Fourteen hours were required for the uptake of 0.046 moles of deuterium gas. The reaction mixture was filtered through a fine-grade sintered-glass funnel under reduced pressure. The resulting colorless solution was diluted to 250 ml. with benzene and oxidized with yellow mercuric oxide (20 grams) by stirring for sixty hours at room temperature. The suspension was filtered through three layers of filter paper (No. 42) and the benzene removed under reduced pressure. Recrystallization of the resulting oil from 40 percent acetone in methanol at -10°C yielded the high-melting form. Recrystallization of the mother liquor from 40 percent acetone in methanol yielded the low-melting form. Further purification of each sample was accomplished by further recrystallization from 40 percent acetone in methanol; HMF, m.p. $146-147^{\circ}\text{C}$ and LMF, m.p. $121-122^{\circ}\text{C}$.

Purification of Benzene

One liter of benzene (Baker reagent grade) was shaken seven times with concentrated sulfuric acid until the acid layer did not turn brown or tan. The benzene was washed with water twice, 6N sodium hydroxide three times until the wash was very basic, and water again until the wash was neutral, dried over anhydrous magnesium sulfate and distilled twice under argon from sodium metal through a 20-inch Vigreux column.

Purification of Ethylbenzene

Eastman reagent grade ethylbenzene was passed through a three-foot column consisting of six inches of acidic alumina at the top, twenty-

four inches of neutral alumina next and six inches of basic alumina at the bottom. The ethylbenzene was then distilled from sodium through a twenty-four-inch Helipak (1/8 inch) column; b.p. 133°C .^{27a}

Kinetic Measurements

The azo compound (approximately 0.024 grams or 0.046 grams) was dissolved in 3 ml. of ethylbenzene and the resulting solution transferred to a fused-quartz ultraviolet cell fitted with a quartz 10/30 inner joint. The solution was degassed at dry ice temperature under high vacuum ($<1 \times 10^{-3}$ torr) by a standard freeze-thaw procedure. The degassing procedure was repeated until the pressure was that of ethylbenzene. The cells were then sealed under vacuum. First-order kinetics were obtained by following the disappearance of the absorption due to the nitrogen-nitrogen bond in a modified Beckman DU spectrophotometer. Infinity readings were taken after a minimum of ten half-lives. Approximately 80-120 points were taken during a run and these were computer-processed to obtain the nonlinear least squares value of the first-order rate constant (see Appendix A). Isotope effects were determined by simultaneously measuring the rates of decomposition of the protiated and deuterated compounds.⁴²

Thermocouple Calibration

The thermocouple was calibrated against a NBS-calibrated thermocouple over the temperature range of the kinetic experiments using a modified Cottrell pump.⁵¹ Liquids used and NBS thermocouple and measuring thermocouple (Ag #2) readings were: benzene, 3.3035, 3.3275; 1,1,2-trichloroethane, 3.5980, 3.6240; iso-octane, 4.170, 4.200; toluene,

4.7005, 4.733; n-octane, 5.413, 5.453; ethylbenzene 5.894, 5.937; n-pentyl acetate, 6.574, 6.6205; bromobenzene, 6.872, 6.927; and t-butylbenzene, 7.594, 7.643 and 7.593, 7.638 (separate measurements).

A plot of EMF (NBS) vs EMF (Ag #2) was not linear over the complete range. However, a linear relationship was followed over two separate ranges and smaller ranges. The slope and intercept and standard deviation of the slope, intercept and y-axis obtained from a linear least squares fit of EMF (NBS) vs. EMF (Ag #2) were 0.9927, 4.849×10^{-4} , 5.685×10^{-4} , 2.465×10^{-3} and 9.722×10^{-4} , for the lower temperature range (78 to 125°C), and 0.9981, -3.428×10^{-2} , 3.528×10^{-3} , 2.464×10^{-2} and 5.009×10^{-3} , respectively for the higher temperature range (134 to 168°C).

Deuterium Content and Correction of Isotope Effect

The deuterium content of Va and XVIa prepared by reduction of the corresponding chloro-azo compounds with lithium aluminum deuteride was determined by combustion.⁵² The deuterium content of Va, XVIIa-HMF, and XVIIa-LMF prepared by reduction of the corresponding azines with gaseous deuterium and oxidation with mercuric oxide was determined by combustion and nmr. The nmr measurements involved a minimum of three independent determinations of the proton ratios for labeled and unlabeled compounds by integration following repetitive scanning with a Varian C-1024.^{27a} Spectra of all samples were taken in chloroform-d (100 atom % D). Comparison of the proton ratios in the labeled compounds, assuming no deuterium in the phenyls, to the corresponding ratios in the unlabeled analogs gave the atom fraction deuterium.^{27b,53}

Equation 18 was used to correct an isotope effect to a maximum

number of atom of \underline{D} . V is the corrected isotope effect, X is the observed isotope

$$V \pm \sigma_V = (X \pm \sigma_X)^{Y \pm \sigma_Y} \quad (6)$$

effect, and $Y \pm \sigma_Y = Z/(W \pm \sigma_W)$ where Z and W are the maximum and experimental number of atoms of D , respectively, at the position of interest. The associated standard deviations are represented by σ_i . For calculations involving data for \underline{Va} (LAD) and \underline{XVIa} (LAD), the standard deviation in the experimental number of atoms of $D(W)$ was replaced by the average deviation. The standard deviation in V was calculated by Equation 19, which was derived from the expression

$$\begin{aligned} \sigma_V &= \pm [(\partial V / \partial X)^2 \sigma_X^2 + (\partial V / \partial Y)^2 \sigma_Y^2]^{1/2} \\ \sigma_V &= \pm V [(Y / \sigma_X)^2 / X^2 + (\sigma_Y \ln X)^2]^{1/2} \end{aligned} \quad (7)$$

PART II. RING DEUTERIUM ISOTOPE EFFECT FOR

1,1'-DI(PHENYL-2,3,4,5,6-d₅)AZOETHANE

CHAPTER I

INTRODUCTION

In a number of free-radical-forming reactions, the logarithms of the relative rates ($\log k_{-X}/k_{-H}$) correlate reasonably well with both σ and σ^+ but the correlation is generally better with σ^+ .⁵⁵ In general, substituents exert a small although non-negligible perturbation upon polarization of the transition state as shown by the magnitude of the ρ values, e.g., decomposition of ring-substituted phenyl peroxyacetates yields a ρ of -1.2 ⁵⁵ and hydrogen atom abstraction from substituted toluenes by trichloromethyl radicals yields a ρ of -1.46 .⁵⁶ Substituent effects have been discussed in terms of their ionic contribution to the ground and/or transition states.

Evidence has been reported which indicates that deuterium is electron-donating relative to hydrogen.⁵⁷ This is deduced from: a) nuclear quadruple coupling constants of deuterated methyl halides,⁵⁸ b) fluorine nmr chemical shifts in deuterated fluorocarbons,⁵⁹ c) the decreased acidity of carbon-deuterated carboxylic acids⁶⁰ (Table XIV), d) the inverse isotope effect for solvolysis of ring-deuterated benzhydryl chloride⁶¹ (Table XV), and e) the inverse equilibrium isotope effect for the formation of deuterated triphenylmethyl cations⁶² (Table XVI).

TABLE XIV

ISOTOPE EFFECTS ON IONIZATION OF CARBOXYLIC ACIDS⁶⁰

Compound	$pK_{\underline{D}} - pK_{\underline{H}}$
DCOOH	0.35 \pm 0.002
CD ₃ COOH	0.014 \pm 0.001
(CD ₃) ₃ CCOOH	0.018 \pm 0.001
C ₆ H ₅ COOH	0.10 \pm 0.002
<u>2,6</u> -D ₂ C ₆ H ₃ COOH	0.003 \pm 0.001

TABLE XV

ISOTOPE EFFECTS IN SOLVOLYSIS OF DEUTERATED BENZHYDRYL
CHLORIDES IN 80% AQUEOUS ACETONE AT 25°C⁶¹

Deuterated Substitution	$\frac{k_{\underline{D}}}{k_{\underline{H}}}$ per \underline{D}
<u>2,6,2',6'</u> -d ₄	1.018 \pm 0.001
<u>3,5,3',5'</u> -d ₄	1.014 \pm 0.001
<u>4,4'</u> -d ₂	1.010 \pm 0.002

TABLE XVI

ISOTOPE EFFECTS ON THE EQUILIBRIUM CONSTANT FOR FORMATION
OF THE RING-DEUTERATED TRIPHENYLMETHYL CATION
FROM TRIPHENYLMETHANOL AT 25°C⁶²

Deuterium Substitution	K_D/K_H per D
2,2',2''-d ₃	1.0133 ± 0.0004
3,3',3''-d ₃	1.0133 ± 0.007
4,4',4''-d ₃	1.0082 ± 0.004

Clearly the decrease in the acidity of carbon-deuterated carboxylic acids is consistent with greater electropositivity of deuterium compared to hydrogen. The data for 2,3,4,5,6-pentadeuterio- and 2,6-dideuterio-benzoic acids lead to the conclusion that all the ring positions contribute approximately equally to the decrease in the acidity of C₆D₅COOH.⁶⁰ The solvolysis of deuterated benzhydryl chloride presents a slightly different picture. Since the development of the positive charge at the ortho and para positions should be greater than at the meta position, one might have anticipated the isotope effect to be more inverse for an ortho or para than for a meta deuterium. However k_D/k_H for an ortho-deuterium is seen in Table XV to be greater than for a para-deuterium. Also, the chemical shifts of ring protons in the triphenylmethyl cation fall in the order para > meta > ortho, which may reflect the relative amount of positive charge at each position.⁶³ From this view point each of the deuterium isotope effects at the

ortho-, meta- and para- positions in the solvolysis of benzhydryl chloride results mainly from the inductive effect of deuterium.⁶¹ The inverse equilibrium isotope effect for ionization of protonated triphenylmethanols is also consistent with a great inductive effect of deuterium relative to hydrogen. Clearly, the isotope effects in the ortho- deuterated compound are not satisfactorily explained solely by relief of nonbonded ground-state interaction between ortho positions in the three rings upon ionization.⁶¹ This explanation would a) require K_H/K_D per ortho- deuterium to be greater than unity and b) predict that K_H/K_D for meta- and para-deuterium would be about unity. Thus the dominant contribution to ring deuterium effects appears to be inductive, with the possibility that the effect at the ortho position is a combination of inductive and steric effects.⁶²

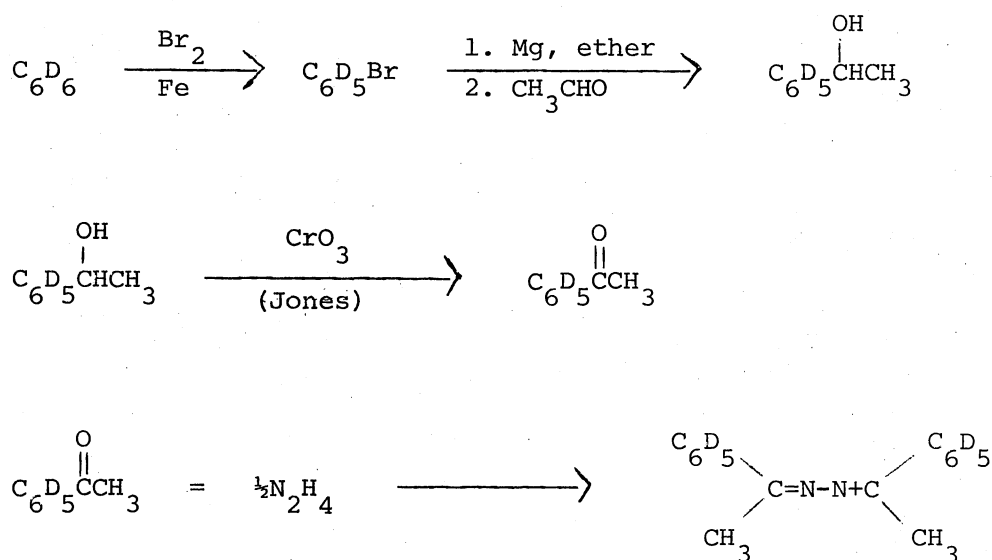
The present work reports an attempt to assess the effect of electron delocalization, in a benzylic free radical, on the aromatic carbon C-H force constants for a radical-forming reaction by measuring the rate of decomposition of 1,1'-di(phenyl-2,3,4,5,6-d₅)azoethane (Vc) relative to 1,1'-diphenylazoethane (V).

CHAPTER II

RESULTS AND DISCUSSION

The synthesis of completely ring-deuterated acetophenone azine was performed via Scheme XVI described by Scheppele and coworkers.⁶⁴

SCHEME XVI



1,1'-Di(phenyl-2,3,4,5,6-d₅)azoethane (Vc) was synthesized by catalytic reduction of acetophenone azine-d₁₀ in two different solvents.^{7,14,21,65} The sample of Vc prepared in 1,4-dioxane was labeled Vc-A and in benzene was labeled Vc-B. The possibility of deuterium loss accompanying catalytic hydrogenation of the azine required the determination of the deuterium content of Vc-A and Vc-B. The atom percent D in the azine pre-

cursor to $\underline{V}_C\text{-A}$ and $\underline{V}_C\text{-B}$ was determined from the M-15 ion region in the 15 and 12.5 e.V. mass spectra of ring-deuterated acetophenone azine⁶⁴ (Table XVII) and found to be 99.5 ± 0.24 percent.⁶⁴ The molecular ion region in the mass spectra of benzoic acid- \underline{d}_5 obtained from the oxidation of $\underline{V}_C\text{-A}$ and $\underline{V}_C\text{-B}$ indicates the presence of 99.41 ± 0.12 and 98.94 ± 0.39 atom percent aromatic deuterium, respectively (Table XVIII). Using 1,4-dioxane as an internal standard, nmr analysis gave 1.966 ± 0.046 and 2.008 ± 0.040 atoms of $\alpha\text{-H}$ for $\underline{V}_C\text{-A}$ and $\underline{V}_C\text{-B}$, respectively (Table XIX). These data suggest, as expected,^{21,66} that within experimental error negligible deuterium exchange accompanies reduction of the deuterated azine.

TABLE XVII
ISOTOPIC PURITY OF ACETOPHENONE AZINE- \underline{d}_{10} FROM THE
M-15 MASS SPECTRAL PEAKS

e.V.	<u>m</u> / <u>e</u>	Ion Intensities ^a	% <u>D</u> ± σ _{%<u>D</u>}
15	231	100.00 ± 0.0	99.49 ± 0.20
	230	4.873 ± 0.088	
	229	0.246 ± 0.031	
12.5	231	100.00 ± 0.0	99.50 ± 0.27
	230	4.818 ± 0.119	
	229	0.192 ± 0.037	
Average % <u>D</u> ± σ _{%<u>D</u>} = 99.50 ± 0.24			

^aCorrected for naturally occurring isotopes and each peak normalized to $\underline{m}/\underline{e}$ 231 = 100.

TABLE XVIII

ISOTOPIC CONTENT OF BENZOIC ACID-d₅ FROM MASS SPECTRA

Benzoic Acid-d ₅ From	e.v.	m/e	Ion Intensities ^a	%D ± σ _{%D}	Average % D ± σ _{%D}
<u>Vc-A</u>	15	127	100.00 ± 0.0		
		126	4.537 ± 0.631	98.75 ± 0.32	
		125	0.978 ± 0.161		98.94 ± 0.39
	12.5	127	100.00 ± 0.0		
		126	3.463 ± 1.005	99.13 ± 0.45	
		125	0.468 ± 1.012		
<u>Vc-B</u>	15	127	100.00 ± 0.0		
		126	2.725 ± 0.116	99.38 ± 0.12	
		125	0.190 ± 0.012		99.40 ± 0.12
	12.5	127	100.00 ± 0.0		
		126	2.752 ± 0.257	99.43 ± 0.12	
		125	0.052 ± 0.037		

^aCorrected for naturally occurring isotopes and each peak normalized to m/e 127 = 100.

TABLE XIX

ISOTOPIC CONTENT OF 1,1'-DIPHENYLAZOETHANE- d_{10} FROM MASS SPECTRA

Compound	α -CH Normalized Ratio	Molar Ratio of Azo Compound to Internal Standard (Dioxane)	α -CH Corrected Intensity	Number of α -H per Molecule
<u>V-A</u>	4.357 ± 0.079	2.1717 ± 0.0043	2.006 ± 0.036	1.966 ± 0.046
<u>Vc-A</u>	4.400 ± 0.065	2.2309 ± 0.0047	1.972 ± 0.029	
<u>V-B</u>	4.081 ± 0.046	2.0391 ± 0.0038	2.001 ± 0.023	2.008 ± 0.0040
<u>Vc-B</u>	3.948 ± 0.064	1.9644 ± 0.0037	2.009 ± 0.033	

The isotope effects were measured by simultaneously observing the rates of decomposition of the protiated (V) and deuterated (Vc-A and Vc-B) azo compounds in ethylbenzene. The average isotope effects and average rate constants are tabulated in Table XX along with the measured temperature. The kinetic data were obtained by observing the changes in the optical density at 360 nm as a function of time. Individual rate constants were calculated by nonlinear least-squares analysis. Equation 5 shows that $k_{\text{H}}/k_{\text{D}}$ is a product of classical mechanical (CM) ($v_{\text{L(H)}}^+/v_{\text{L(D)}}^+$) and quantum mechanical (QM) (VP x EXC x ZPE) terms.

$$\frac{k_{\text{H}}}{k_{\text{D}}} = (v_{\text{L(H)}}^+/v_{\text{L(D)}}^+) \times \text{VP} \times \text{EXC} \times \text{ZPE} \quad (5)$$

The observed rates of pyrolysis of 1,1'-(3,3'- and 4,4'-disubstituted) diarylazoethanes are listed in Table XXI. Linear least squares plot of $\log (k_{\text{X}}/k_{\text{H}})$ as a function of σ^+ and σ yields ρ values of -0.095 ± 0.007 and -0.275 ± 0.056 at 104.57°C respectively.

Hammett's linear free-energy relationship is defined as

$$\log (k_{\text{X}}/k_{\text{H}}) = \rho \sigma_{\text{i}} \quad (6)$$

where k_{X} is the rate constant for a given reaction of a compound containing substituent X, k_{H} is the rate constant for the same reaction for the unsubstituted compound, ρ is the reaction constant for a given reaction and σ_{i} is a constant for a given substituent X.⁶⁷ The σ values have been derived by studying the ionization of substituted benzoic acids, where ρ is defined as one.⁶⁸ The σ^+ values have been derived by studying the solvolysis of substituted cumyl chlorides, where ρ is defined as one.⁶⁹ By using the ρ values for decomposition of V and the

TABLE XX

 RING DEUTERIUM ISOTOPE EFFECT IN THE DECOMPOSITION
 OF 1,1'-DIPHENYLAZOETHANES

Compound	Temperature, °C	$k \times 10^5, \text{min}^{-1}$ ^a	$k_{\text{H}}/k_{\text{D}}$ ^b
<u>V</u>	104.58 ± 0.06	4.979 ± 0.074	1.030 ± 0.007 ^{c,d}
<u>VC-A</u>		4.834 ± 0.049	
<u>V</u>	104.57 ± 0.06	5.059 ± 0.030	1.030 ± 0.008 ^e
<u>VC-B</u>		4.913 ± 0.033	

^a Average rate constants.

^b Average of several isotope effect determinations.

^c Seven of eight determinations.

^d $k_{\text{H}}/k_{\text{D}}$ at 113.62 ± 0.06°C is 1.034 ± 0.002 (two determinations).

^e Five of five determinations.

TABLE XXI

RATE CONSTANTS FOR DECOMPOSITION OF RING-SUBSTITUTED 1,1'-DIPHENYLAZOETHANES^a

Substituent X	$k \times 10^3, \text{ min}^{-1}$					Rel. Rate at 104.57°C	σ^b	σ^{+b}
	100.4°C	110.3°C	105.13°C	105.35°C	112.91°C			
H	3.27	10.14		5.447	12.80	1.0	0.0	0.0
<u>m</u> -CH ₃				5.443	12.87	1.0	-0.069	-0.66
<u>p</u> -CH ₃	3.54	11.10	6.146		14.65	1.336	-0.171	-0.311
<u>p</u>	4.29	14.88	7.372		17.57	1.627	-0.268	-0.778
						$\rho(\sigma^+) = -0.095 \pm 0.007$		
						$\rho(\sigma) = -0.275 \pm 0.056$		

^aRate constants at 100.4 and 110.3°C are from Ref. 7b and rate constants at 105.13, 105.35 and 112.91°C are from Ref. 65.

^bH. C. Brown and Y. Okamoto, J. Amer. Chem. Soc., **80**, 4979 (1958).

solvolysis of benzhydryl chlorides XXX (-4.03^{70}) and the isotope effects for the solvolysis of ortho-, meta- and para-deuterated benzhydryl chloride, ring deuterium isotope effect for the decomposition of

V ($k_{\underline{V}}/k_{\underline{Vc}}$) was calculated from the following equation:

$$\log \left(\frac{1}{\frac{k_{\underline{H}}}{k_{\underline{D}}} \frac{k_{\underline{V}}}{k_{\underline{Vc}}}} \right) = \frac{\rho_{\underline{V}}}{\rho_{\underline{XXX}}} \log \left(\frac{1}{\frac{k_{\underline{H}}}{k_{\underline{D}}} \frac{k_{\underline{XXX}}}{k_{\underline{Vc}}}} \right) \quad (9)$$

The ring deuterium isotope effects for the solvolysis of XXX predicts $k_{\underline{H}}/k_{\underline{D}}$ values of 0.9946 and 0.9968 for ρ values of -0.095 and -0.275 respectively which do not agree with the experimental value of 1.030 as shown in Table XXII.

TABLE XXII

RING DEUTERIUM ISOTOPE EFFECTS FOR SOLVOLYSIS OF BENZYHYDRYL CHLORIDE AND CALCULATED ISOTOPE EFFECTS FOR THE THERMOLYSIS OF V/Vc

Position of D	$(\frac{k_{\underline{H}}}{k_{\underline{D}}})_{\underline{XXX}}$	$(\frac{k_{\underline{H}}}{k_{\underline{D}}})_{\underline{V}}$ at 104.57°C	
		$\rho = -0.095$	$\rho = -0.275$
Ortho	.9823	.9988 ^a	.9996 ^a
Meta	.9862	.9990 ^a	.9997 ^a
Para	.9901	.9993 ^a	.9998 ^a
Total for <u>V/Vc</u>		.9946 ^b	.9968 ^b

^aPer atom D.

^bFor 10 atoms deuteriums.

This disagreement between the calculated and experimental isotope

effects for $\underline{V}/\underline{V}_c$ may result from the possibility that the classical mechanical portions of $k_{\underline{H}}/k_{\underline{D}}$ may not correlate with σ or σ^+ values. For $\underline{XXX}/\text{ring-deuterio-}\underline{XXX}$ per \underline{D} the separating-mass-fragment approximation yields a value of 1.001 for $\underline{V}_{L(H)}^+/\underline{V}_{L(D)}^+$). From Equation 5 the quantum mechanical contribution to the isotope effect is given by $(k_{\underline{H}}/k_{\underline{D}})/(\underline{V}_{L(H)}^+/\underline{V}_{L(D)}^+)$. Without further justification the equation for estimation of the quantum mechanical portion of $\underline{V}/\underline{V}_c$ is

$$\log \left(\frac{1}{Q_M} \right) \underline{V} = \frac{\rho \underline{V}}{\rho \underline{XXX}} \times \log \left(\frac{1}{Q_M} \right) \underline{XXX} \quad (10)$$

Equation 10 yields values of 0.9990 and 0.9894 for the quantum mechanical portion of $\underline{V}/\underline{V}_c$, see Table XXIII.

TABLE XXIII

RING DEUTERIUM ISOTOPE EFFECTS FOR SOLVOLYSIS OF BENZHYDRYL CHLORIDE AND CALCULATED QUANTUM MECHANICAL EFFECTS FOR $\underline{V}/\underline{V}_c$

Position of D	$(k_{\underline{H}}/k_{\underline{D}})_{\underline{XXX}}^{a,b}$	(VP x EXC x ZPE) \underline{XXX}	(VP x EXC x ZPE)	
			$\rho = -0.095$	$\rho = -0.275$
Ortho	0.9823	0.9813	0.99999 ₆ ^b	0.9987 ^b
Meta	0.9862	0.9852	0.99964 ₈ ^b	0.9900 ^b
Para	0.9901	0.9891	0.99974 ₂ ^b	0.9993 ^b
Total for $\underline{V}/\underline{V}_c$			0.9981 ^c	0.9894 ^c

^aData for 70 and 80% aqueous acetone 25°C.

^bPer atom \underline{D} .

^cFor ten atoms of \underline{D} .

These results clearly indicate that the delocalization of the incipient odd electron in the transition state for V results in a negligible perturbation of the aromatic carbon-hydrogen force constants for $\underline{V/V_C}$.

The separating-mass-fragment approximation⁷¹ yields a value of 1.024 for

$$\underline{v_{L(H)}^+}/\underline{v_{L(D)}^+}, \text{ i.e., } v_{L(H)}^+/v_{L(D)}^+ = \left(\frac{1}{m_{Y-H}} / \frac{1}{m_{Y-D}} \right)^{1/2},$$

where m_{Y-H} and m_{Y-D} are the masses of $C_6H_5CHCH_3$ and $C_6D_5CHCH_3$, respectively. This value may be regarded as a lower limit to the correct value. For example, for \underline{V} methyl- d_6 the "exact" value for $v_{L(H)}^+/v_{L(D)}^+$ (1.026) is larger than the value from the separating-mass-fragment approximation model (1.014).⁴² Tentatively and without attempt at justification, an alternative value of 1.044, i.e., $(1.026)^{10/6}$, is assumed for $v_{L(H)}^+/v_{L(D)}^+$ for $\underline{V/V_C}$. The measured isotope effect for $\underline{V/V_C}$ (1.030) is encompassed by the range of 1.024-1.044. Table XXIV lists the values of $v_{L(H)}^+/v_{L(D)}^+$ for $\underline{V/V_C}$ computed from the values of VP x EXC x ZPE with the value of $k_{\underline{H}}/k_{\underline{D}} \pm \sigma_{k_{\underline{H}}/k_{\underline{D}}}$. The calculated and the experimentally determined ranges of $v_{L(H)}^+/v_{L(D)}^+$ are in reasonable agreement within the limits of experimental error, 1.025-1.039 and 1.034-1.048, respectively.

With the agreement achieved using Equation 10 it must be concluded that the classical mechanical portion of Equation 5 does not and should not correlate well within the framework of Hammett's equation because of being basically mass resultant.

TABLE XXIV

EXPERIMENTAL RANGE OF $\nu_{L(H)}^+/\nu_{L(D)}^+$ for γ/γ_c

ρ	$k_{\underline{H}}/k_{\underline{D}}$	VP x EXC x ZPE	$(\nu_{L(H)}^+/\nu_{L(D)}^+)$ exptl
0.095	1.037	0.9981	1.039
	1.030		1.032
	1.023		1.025
0.275	1.037	0.9894	1.048
	1.030		1.041
	1.023		1.034

CHAPTER III

EXPERIMENTAL

Preparation of Bromobenzene- d_5 ⁶⁴

Benzene- d_6 (Merck, Sharp and Dohme, indicated isotopic purity 99.5 atom percent d ; 45 g., 0.536 mole) was treated with bromine (80 g., 0.50 mole) in the presence of iron. The crude product was taken up in ether and washed with water, saturated sodium bicarbonate solution and water, the ether solution dried and filtered and the ether removed under reduced pressure. Distillation at atmospheric pressure yielded 39.1 g. of bromobenzene- d_5 , 49.1 percent yield; b.p. $152\text{--}153^\circ\text{C}$ (lit. $156\text{--}158^\circ\text{C}$).⁷²

Preparation of Acetophenone- d_5 ⁶⁴

Acetaldehyde (10.48 g., 0.238 moles) dissolved in 50 ml. of ether (distilled from lithium aluminum hydride) was added to phenylmagnesium bromide- d_5 prepared from magnesium turnings (5.35 g., 0.238 moles) and bromobenzene- d_5 (38.50 g., 0.288 moles) in 50 ml. of ether (distilled under argon from lithium aluminum hydride into the reaction flask). The cooled (ice bath) reaction mixture was hydrolyzed by slow addition of 10 percent hydrochloric acid. The reaction mixture was extracted with ether and the extract washed with saturated sodium bicarbonate solution and water, dried, filtered and freed from ether under reduced pressure. Distillation at reduced pressure (20 mm) yielded 29.3 g. of 1-phenylethanol- d_5 , b.p. $101\text{--}102^\circ\text{C}$. The 1-phenylethanol- d_5 was oxidized at low

temperature (ice bath) with chromium trioxide.⁷³ Distillation at 17 mm pressure yielded 14.2 g. (49.7 percent yield) of acetophenone- d_5 ; b.p. 78-79°C. (lit. 78°C)⁷⁴.

Preparation of Acetophenone Azine- d_{10} ⁶⁴

Acetophenone- d_5 (13.8 g., 0.11 moles) was converted to the azine by the procedure previously used for XXIV; m.p. 121-122°C.

Preparation of 1,1'-Di(phenyl-2,3,4,5,6- d_5)- azoethane (Vc)^{21,65}

Method a

Five percent palladium-on-carbon (1.1 g.) suspended in 50 ml. of 1,4-dioxane (distilled under argon from lithium aluminum hydride directly into the hydrogenation flask) was equilibrated with deuterium gas. Acetophenone azine- d_{10} (4 g., 0.0161 moles) was reduced at atmospheric pressure until the required uptake of two moles of deuterium gas per mole of azine was completed. The reaction mixture was filtered through a fine-grade sintered-glass funnel and the dioxane was removed under reduced pressure. The colorless liquid hydrazine was dissolved in 250 ml. of benzene and oxidized, with continuous stirring, by addition of yellow mercuric oxide in 20-g. portions until no change in the added mercuric oxide was observed (60 g. used over a 2-hour period). The mixture was filtered through three layers of No. 1 filter paper and the benzene removed under reduced pressure. The crude azo compound are repetitively recrystallized from methanol and once from hexane and then dried under vacuum; m.p. 71-72.5°C; ϵ (benzene) 45.12, λ_{max} 360 m μ .

Method b

The same procedure was followed except that the reduction was carried out in purified benzene. The benzene was distilled under argon from sodium directly into the hydrogenation flask; product m.p. 71.2-71.7°C.

Isotope Effect Determination

The isotope effects were determined by simultaneously measuring the rates of decomposition of the protium and deuterium compounds in the same cell compartment of a modified Beckman DU spectrophotometer^{21,27a,65}.

Oxidation of 1,1'-Di(phenyl-2,3,4,5,6-d₅)- azoethane to Benzoic Acid-d₅

The deuterated azo compound (0.1 g., 0.0004 moles) and chromium trioxide (0.5 g., 0.005 moles) were dissolved in 30 ml. of glacial acetic acid and the solution refluxed 90 minutes. The reaction mixture was cooled and diluted with an equal volume of distilled water and the aqueous mixture continuously extracted with n-pentane for forty-eight hours. The pentane was evaporated and the benzoic acid was recrystallized from water; m.p. 120-121°C.

Deuterium Content

Mass Spectrometric Method

Mass spectra were recorded at 15 and 12.5 e.V. (nominal) on an LKB 9000 mass spectrometer. Spectra were obtained by introducing samples of the azine through the separators and benzoic acid-d₅ through the heated

glass inlet. The ion source temperature was 310°C . The isotopic purity for each sample was calculated after the spectra were corrected for naturally occurring heavy isotopes.⁶⁴

Nuclear Magnetic Resonance Method

The deuterium content was determined by repetitively integrating single-scan nmr spectra of V, Vc-A and Vc-B in chloroform- d_5 (100 atom percent- d) containing 1,4-dioxane as an internal standard. A mole ratio of azo compound to 1,4-dioxane of approximately 1 to 4 was chosen so that the area under the quartet due to the methinyl protons approximated the area for the singlet due to the 1,4-dioxane protons. The nmr measurements were made using a Varian HA-60 spectrometer.⁷⁵ The integral heights for each peak were normalized and the deuterium content for the alpha position was calculated.

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A P P E N D I X E S

APPENDIX A

COMPUTATION OF FIRST ORDER RATE CONSTANTS USING A NONLINEAR LEAST SQUARES TECHNIQUE

APPENDIX A

COMPUTATION OF FIRST ORDER RATE CONSTANTS USING

A NONLINEAR LEAST SQUARES TECHNIQUE

Rate constants were obtained by fitting optical density (O.D.) data to an equation of the form

$$Y = A + Be^{-kX}$$

by a nonlinear least squares technique, where Y is O.D., at any time X, A is O.D. at infinite time (O.D. after 10 half lives), B is O.D. at $t = 0$ minus A, and k is the rate constant. The computer program requires initial estimates of A, B, and k. The estimates were obtained from a semi-log plot of O.D. versus time.

Computer program control and data cards are punched as follows:

1. First control card

<u>Column</u>	<u>Format</u>	
1-6	16	Problem number
7-12	16	Number of observations
13-26	E14.7	Estimate of A
27-40	E14.7	Estimate of B
41-54	E14.7	Estimate of k
55-57	13	PRNT 0 for printout of Y calc.

2. Second card, columns 1-80 in A format put label for data.

3. Data cards containing no more than 200 points.

<u>Column</u>	<u>Format</u>	
1-12	F12.6	O.D.
13-24	F12.6	Time

4. More than one kinetic data set can be separately processed.

After the last data set a card with zeros in column 7-12 is added.

The program will reject points which deviate more than 2.17σ from O.D. calculated. Only one point is rejected per iteration. The program yields a final of A, B and k in the last iteration.

APPENDIX B

TABULATION OF RATE DATA FOR PART I

APPENDIX B

TABULATION OF RATE DATA FOR PART I

Compound	Labile X	Measured EMF, mV	$k \times 10^3 \text{ min}^{-1}$	Temp. °C	Average $k \times 10^3 \text{ min}^{-1}$
<u>V-A</u> and <u>Va-A</u>	H	4.463	4.5287	103.90 ± 0.04	
	D		3.8055		
	H	4.461	4.4903		
	D		3.7825		
	H	4.461	4.4743		
	D		3.7195		
	H	4.461	4.4648		
	D		3.7556		
	H	4.462	4.5304		
	D		3.797		
	H	4.462	4.5049		
	D		3.7992		
	H	4.462			4.4989
	D	4.462			3.7767
<u>V-B</u> and <u>Va-B</u>	H	4.461	4.5176	103.90 ± 0.2	
	D		3.9087		
	H	4.467	4.5762		
	D		3.9612		
	H	4.460	4.5166		
	D		3.8566		
	H	4.460	4.5642		
	D		3.9041		
	H	4.460	4.5727		
	D		3.9737		
	H	4.462			4.5495
	D	4.462			3.9221

APPENDIX B (Continued)

Compound	Labile X	Measured EMF, mV	$k \times 10^3 \text{ min}^{-1}$	Temp. °C	Average $k \times 10^3 \text{ min}^{-1}$
<u>XVII-HMF</u>	H	4.565	7.0603		
	D		6.1500		
	H	4.565	7.0061		
	D		6.1006		
	H	4.563	6.8370		
	D		6.0007		
	H	4.563	6.8604		
	D		6.0401		
	H	4.563	6.9965		
	D		6.0880		
	H			106.07 ± 0.06	6.9521
	D			106.07 ± 0.06	6.0763
	H	4.0935	1.9630		
	H		1.9329		
				95.97 ± 0.06	1.9480
	H	4.964	18.1214		
	H		18.3025		
				114.51 ± 0.07	18.2119
	D	4.940	17.0945		
			17.4201		
	H	4.938	16.7383		
			16.7687		
				113.98 ± 0.05	17.0054
<u>XVII-LMF</u>	H	4.510	10.4324		
	D		8.5593		
	H	4.511	10.4085		
	D		8.6401		
	H	4.510	10.4425		

APPENDIX B (Continued)

Compound	Labile X	Measured EMF, mV	$k \times 10^3 \text{ min}^{-1}$	Temp. °C	Average $k \times 10^3 \text{ min}^{-1}$
	D		8.6159		
	H	4.508	10.2281		
	D		8.4775		
				104.91 ± 0.06	10.3779
				104.91 ± 0.06	8.5732
<u>XVII-LMF</u>	H	4.0925	3.6212		
	H		3.6442	95.97 ± 0.04	3.6327
	H	4.980	30.8173		
	H		30.9636		
	H	4.980	29.7051		
	H		30.3130	114.85 ± 0.06	30.4497
<u>XVI</u>	H	6.100	1.9940		
	D		1.6553		
	H	6.100	2.0203		
	D		1.6852		
	H	6.094	2.0006		
	D		1.6768		
	H	6.098	1.9807	137.84 ± 0.19	1.9989
	D		1.6509	137.89 ± 0.19	1.6671
	H	6.710	8.0232		
	D		6.8019		
	H	6.710	8.0447		
	D		6.9963		
	H	6.711	8.1043		
	D		6.9531		
	H	6.712	8.0914		
	D		6.8046		

APPENDIX B (Continued)

Compound	Labile X	Measured EMF, mV	$k \times 10^3 \text{ min}^{-1}$	Temp. °C	Average $k \times 10^3 \text{ min}^{-1}$
	H	6.711	8.0653	150.26 ± 0.16	8.0658
	D		6.8525	150.26 ± 0.16	6.8817
	H	7.112	18.7132		
	D		16.0836		
	H		18.6905		
	D		16.2516		
	H		18.4437		
	D		15.8301		
	H		18.4482		
	D		16.0605		
	H		18.3063	158.27 ± 0.20	18.5204
	D	7.112	15.7915	158.27 ± 0.20	16.0035

APPENDIX C

DEUTERIUM ANALYSIS DATA

APPENDIX C

DEUTERIUM ANALYSIS DATA

Combustion Analysis

Compound	Atom % D	Number D
$\begin{array}{c} \text{D} \quad \text{D} \\ \quad \\ \text{Ø}-\text{C}-\text{N}=\text{N}-\text{C}-\text{Ø} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$		
(<u>Va-A</u>)	10.88 and 10.90	1.9602 ± 0.0018
(<u>Va-B</u>)	10.07 and 10.04	1.585 ± 0.016
$\begin{array}{c} \text{D} \quad \text{D} \\ \quad \\ \text{Ø}-\text{C}-\text{N}=\text{N}-\text{C}-\text{Ø} \\ \quad \\ \text{C}(\text{CH}_3)_3 \quad \text{C}(\text{CH}_3)_3 \end{array}$		
<u>XVIa</u>	6.65 and 6.67	1.998 ± 0.003
$\begin{array}{c} \text{D} \quad \text{D} \\ \quad \\ \text{Ø}-\text{C}-\text{N}=\text{N}-\text{C}-\text{Ø} \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{CHØ}_2 \quad \text{CHØ}_2 \end{array}$		
(<u>XVIIa-HMF</u>)	3.94 and 3.97	1.5029 ± 0.0057
(<u>XVIIa-LMF</u>)	3.99 and 3.95	1.5086 ± 0.0076
$\left[\begin{array}{c} \text{D} \\ \\ \text{Ø}-\text{C}-\text{N}= \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array} \right]_2$	a 6.43 and 6.46	1.6758 ± 0.002
	b 6.65 and 6.62	1.7252

APPENDIX C (Continued)

Compound	Atom % D	Number D
$\left[\begin{array}{c} \text{D} \\ \\ \text{C}-\text{N}= \\ \\ \text{CH}_2 \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array} \right]_2$	a 10.96 and 10.92	2.4068 \pm 0.004
	b 8.24 and 10.27	1.8161 \pm 0.003

N.M.R. Analysis

Compound	Labile X	Type Integration*	Normalized Peak Areas**			
			\emptyset	α -CH	γ -CH	β -CH ₂
$\left[\begin{array}{c} \text{X} \\ \\ \text{C}-\text{N}= \\ \\ \text{CH}_2 \\ \\ \text{CH}\emptyset \end{array} \right]_2$ <u>HMF</u>	D	TA	15.0	0.2630 ± 0.0072	1.0456 ± 0.00	2.0926 ± 0.0126
	D	TA		0.2745 ± 0.0034	1.0179 ± 0.0055	2.0 \pm
	H	TA	15.0	0.034 ± 0.0322	1.0227 ± 0.0282	2.0138 ± 0.0315
	H	TA		1.0035 ± 0.0041	1.0000 ± 0.0033	2.0
	D	DI	15.0	0.2681 ± 0.0127	0.9968 ± 0.0234	1.920 ± 0.0467
	D	DI		0.2738 ± 0.0115	1.0186 ± 0.0274	2.0
	H	TA	15.0	0.9714 ± 0.0126	0.9655 ± 0.0142	1.9167 ± 0.0355
	H	TA		0.9880 ± 0.0072	0.9982 ± 0.0113	2.0
<u>LMF</u>	D	TA	15.0	0.2193 ± 0.0114	0.9060 ± 0.1755	1.8869 ± 0.0314
	D	TA		0.2528 ± 0.0044	0.9611 ± 0.0079	2.0

APPENDIX C (Continued)

Compound	Labile X	Type Integration*	Normalized Peak Areas**			
			ϕ	α -CH	γ -CH	β -CH ₂
	H	DI	15.0	0.9994 ± 0.0178	1.0078 ± 0.0181	2.0008 ± 0.0245
		DI		1.0090 ± 0.0377	0.9724 ± 0.0249	2.0
	D	DI	15.0	0.2559 ± 0.0266	0.9494 ± 0.0516	1.9896 ± 0.0792
	D	DI		0.2596 ± 0.0146	0.9321 ± 0.0301	2.0

Compound	Labile X	Sample	Normalized Peak Areas**		
			ϕ	α -CH	β -CH ₂
$\left[\begin{array}{c} \text{X} \\ \\ \phi - \text{C} - \text{N} = \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array} \right]_2$	H		10	1.8173 \pm 0.0159	4.1746 \pm 0.0227
			10	1.8432 \pm 0.0186	4.2226 \pm 0.0381
			10	1.8712 \pm 0.0117	
			10	1.9014 \pm 0.0207	
			10	1.9411 \pm 0.0251	
			10	1.9435 \pm 0.0167	
			10	1.9381 \pm 0.0733	
			10	1.9058 \pm 0.0482	4.7880 \pm 0.0694
			10	1.9329 \pm 0.0129	
			10	1.9253 \pm 0.0050	
			10	1.9671 \pm 0.0219	
			10	1.9370 \pm 0.0200	4.5817 \pm 0.0110
			10	1.8767 \pm 0.0144	
			10	1.8663 \pm 0.3420	
	D	a	10	1.9193 \pm 0.0314	
			10	1.9137 \pm 0.1408	
			10	0.2795 \pm 0.0336	
			10	0.3280 \pm 0.0125	
			10	0.2310 \pm 0.0368	4.1281 \pm 0.0440
			10	0.3224 \pm 0.0075	
			10	0.3067 \pm 0.0324	
			10	0.2580 \pm 0.0197	4.1595 \pm 0.0247
			10	0.3032 \pm 0.0319	
			10	0.2954 \pm 0.0071	
			10	0.2797 \pm 0.0149	
		b	10	0.2612 \pm 0.0075	
			10	0.2597 \pm 0.0131	4.5904 \pm 0.0344

APPENDIX C (Continued)

Compound	Labile X	Sample	Normalized Peak Areas**		
			ϕ	α -CH	β -CH ₂
			10	0.2682 \pm 0.0304	
			10	0.2749 \pm 0.0115	
$\left[\begin{array}{c} \text{X} \\ \\ \phi - \text{C} - \text{N} = \\ \\ \text{CH}_2 \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array} \right]_2$	H		10	1.8682 \pm 0.0156	
	H		10	1.8734 \pm 0.0293	3.7893 \pm 0.0337
	H		10	1.8914 \pm 0.0250	3.8031 \pm 0.0160
	H		10	1.8466 \pm 0.0246	3.8526 \pm 0.0206
	H		10	2.0169 \pm 0.0343	
	H		10	2.0097 \pm 0.0417	
	H		10	2.0143 \pm 0.0153	4.1773 \pm 0.0314
	D	a	10	0.2493 \pm 0.0616	3.6559 \pm 0.0615
	D	a	10	0.3122 \pm 0.0133	
	D	a	10	0.2603 \pm 0.0151	
	D	a	10	0.2460 \pm 0.0246	3.4571 \pm 0.0099
	D	a	10	0.2540 \pm 0.0137	3.7105 \pm 0.0190
	D	b	10	0.2317 \pm 0.0137	3.8422 \pm 0.0149
	D	b	10	0.2236 \pm 0.0086	
				0.2007 \pm 0.0027	
	D	b	10	0.2034 \pm 0.0147	3.7943 \pm 0.0273
				0.2004 \pm 0.0196	3.8300 \pm 0.0101
				0.2073 \pm 0.0106	3.8731 \pm 0.0151
				0.1959 \pm 0.0255	3.8366 \pm 0.0182
				0.2138 \pm 0.0086	

APPENDIX C (Continued)

Compound	Labile X	Azo g.	CDCl ₃ g.	Dioxane g.	Dioxane	Normalized Peak Areas**		
						Ø	α-CH	CH ₃
$\left[\begin{array}{c} \text{H} \\ \\ \text{C}_6\text{X}_5\text{C}-\text{N}=\text{CH}_3 \end{array} \right]_2$	H	0.3000	0.5909	0.0711	8.00	15.1522 ± 0.2372	3.1775 ± 0.0565	9.1034 ± 0.1092
					8.00	15.2124 ± 0.1234	3.1965 ± 0.0290	9.0915 ± 0.0881
					8.00		3.1849 ± 0.0574	9.2001 ± 0.0804
	H	0.3000	0.5164	0.0567	8.00	18.6299 ± 0.1271	3.8871 ± 0.0468	11.3199 ± 0.0628
					8.00		3.8027 ± 0.0354	11.3193 ± 0.0918
					8.00	23.5140 ± 0.1883	4.8684 ± 0.0530	14.2745 ± 0.0987
	H	0.3002	0.5137	0.0468	8.00		4.8764 ± 0.1016	14.3355 ± 0.2562
					8.00	23.4299 ± 0.2321	4.8373 ± 0.0592	14.1399 ± 0.1913
					8.00		4.7312 ± 0.0750	14.1781 ± 0.2455
	D	0.3000	0.5560	0.0477	8.00		4.3883 ± 0.0626	13.4711 ± 0.1593
					8.00		4.4001 ± 0.0649	13.5431 ± 0.1154
					8.00		4.0641 ± 0.0643	12.4466 ± 0.0872
	H	0.3001	0.5247	0.0511	8.00		4.3471 ± 0.0788	13.0615 ± 0.2089
	H	0.3002	0.5168	0.0488	8.00		4.6275 ± 0.0511	14.3108 ± 0.4567
	D	0.2996	0.5168	0.0541	8.00		3.9475 ± 0.0635	12.1195 ± 0.1874
	H	0.2995	0.5149	0.0543	8.00		4.0806 ± 0.0462	12.6426 ± 0.0488

Note: All other n.m.r. measurements were discarded because of phase setting was not correct.

*TA indicates time-averaging integration: DI indicates direct integration.

**Normalized peak area carry additional digit for computational purposes.

APPENDIX D

THERMOCOUPLE CALIBRATION

APPENDIX D
THERMOCOUPLE CALIBRATION

Data for Thermocouple

Boiling Liquid	NBS Thermocouple Readings in mV	Measuring Thermocouple Reading in mV	EMF Measuring Thermocouple (x) vs Thermocouple (y)	
			Slope	Intercept
<u>Temperature Range 80-125°C</u>				
Benzene	3.3035	3.3275		
1,1,2-Trichloroethane	3.5980	3.6240		
Iso-octane	4.1700	4.2000		
Toluene	4.7005	4.7330		
<u>n</u> -Octane	5.4130	5.4531	0.992739 ±0.000569	0.000485 ±0.002465
<u>Temperature Range 135-168°C</u>				
Ethylbenzene	5.8940	5.9370		
<u>n</u> -Pentyl acetate	6.5740	6.6205		
Bromobenzene	6.8720	6.9270		
<u>t</u> -Butylbenzene	7.5940 (7.593)*	7.6430 (7.6380)*	0.998070 ±0.003528	-0.034279 ±0.024640

*Second measurement.

APPENDIX E

MASS SPECTRAL MEASUREMENT OF AZINES

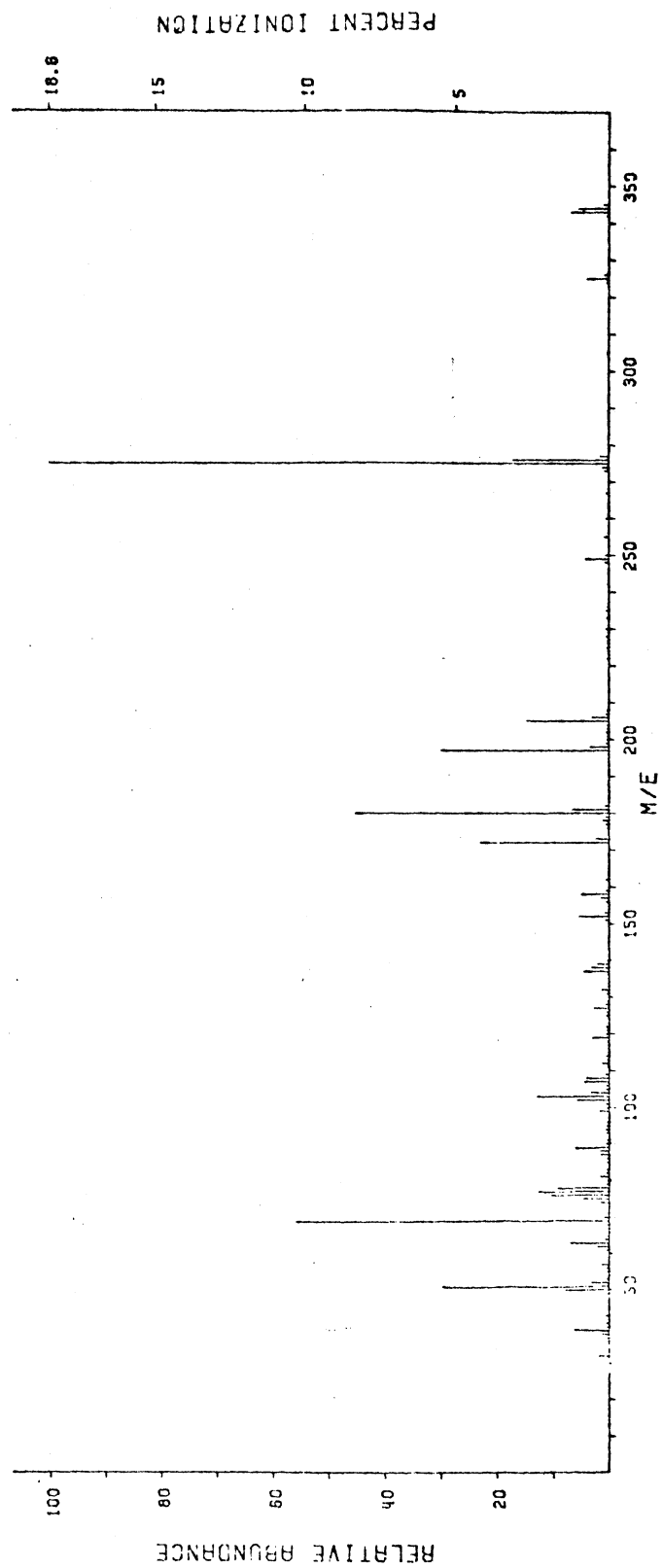
APPENDIX E

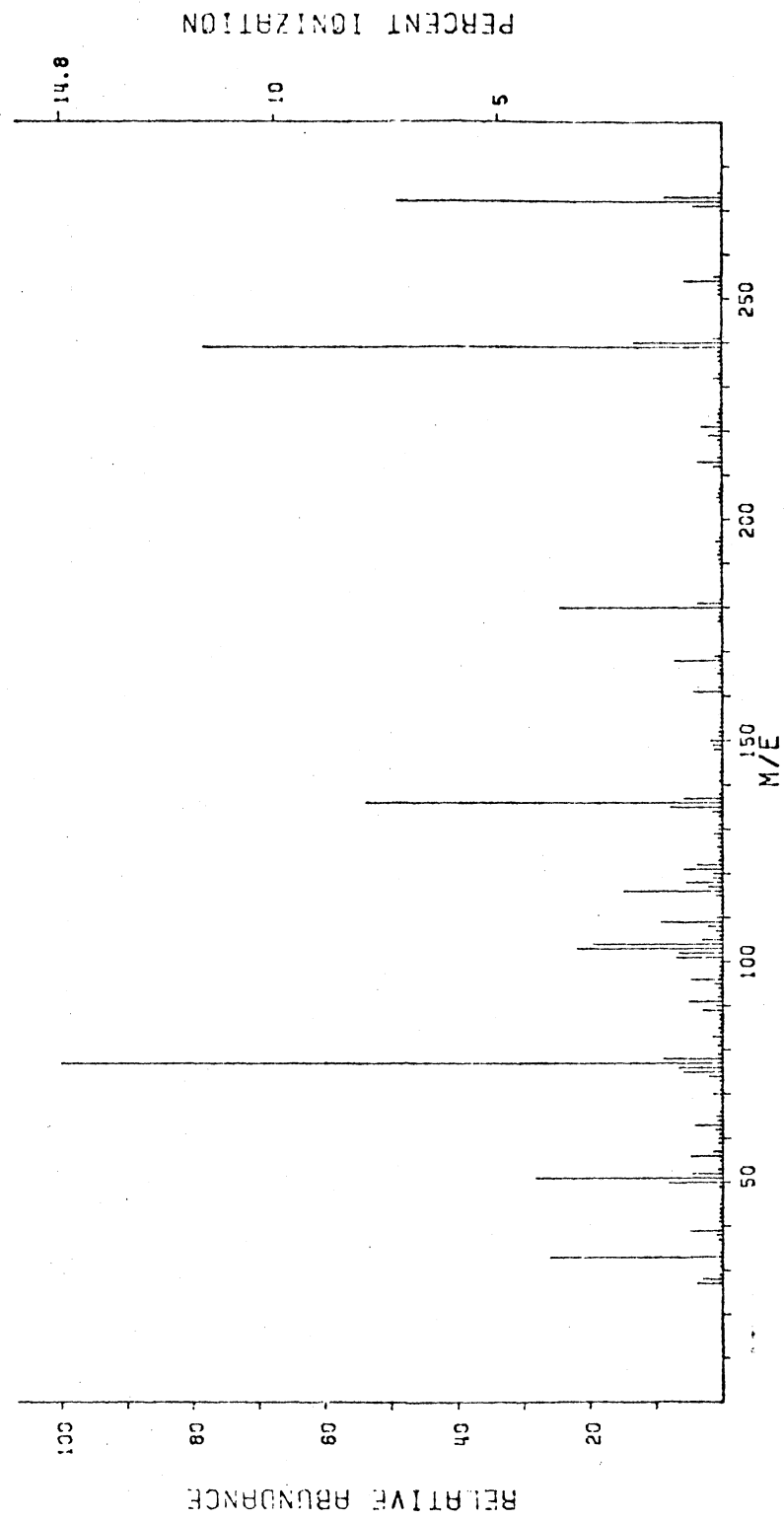
MASS SPECTRAL MEASUREMENT OF AZINES

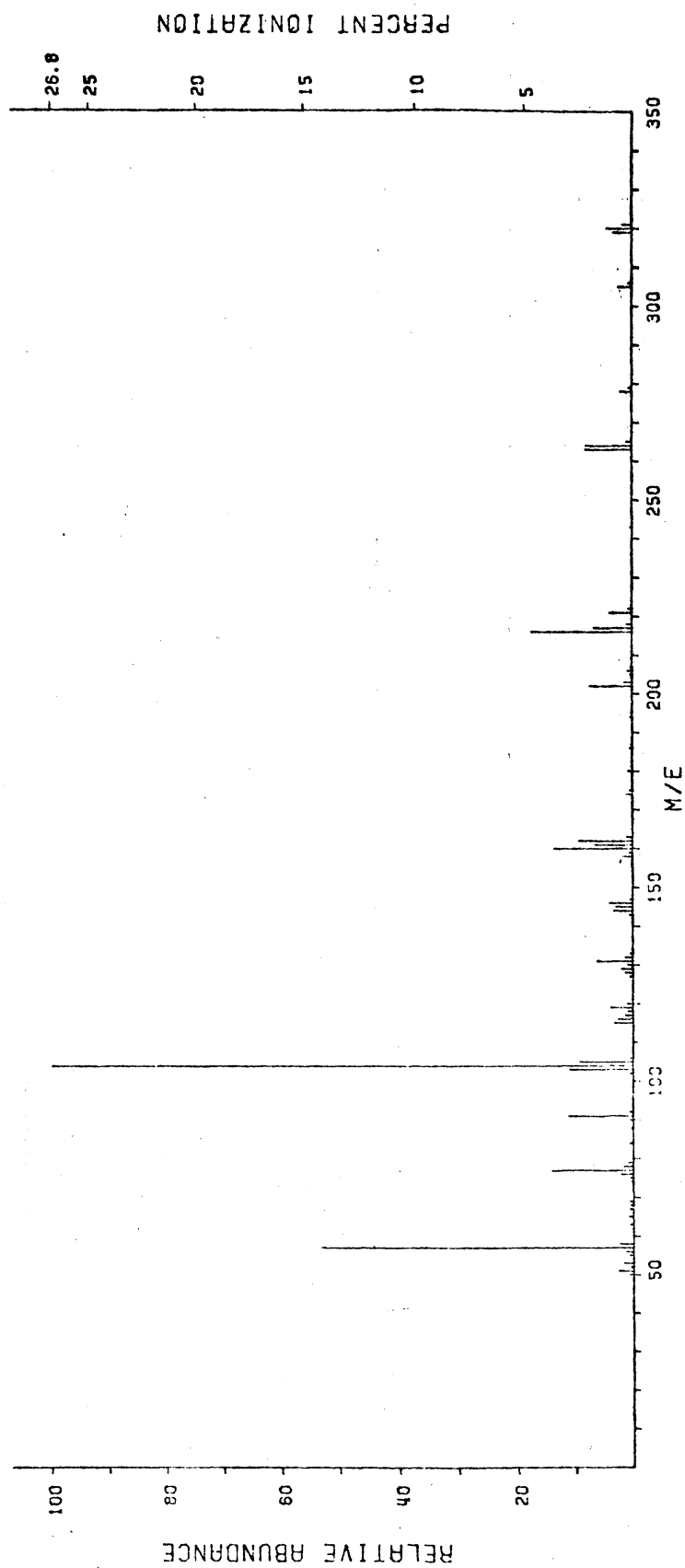
Compound	<u>m/e</u>	Composition	Calculated Mass	Measured Mass	Δm
$\left[\begin{array}{c} \phi - C=N- \\ \\ CH_3 \\ \\ C \\ / \quad \backslash \\ CH_3 \quad CH_3 \end{array} \right]_2$	320	$C_{22}H_{28}N_2$	320.2252	320.2229	2.3×10^{-3}
	319	$C_{22}H_{21}N_2$	319.2174	319.2193	1.8×10^{-3}
	263	$C_{18}H_{19}N_2$	263.1548	263.1548	1.1×10^{-4}
$\left[\begin{array}{c} \phi \\ \\ C=N- \\ \\ CH_2 \\ \\ \phi - C - \phi \\ \\ H \end{array} \right]_2$	568	$C_{42}H_{36}N_2$	568.2878	568.2880	2.1×10^{-4}
	387	$C_{28}H_{23}N_2$	387.1861	387.1852	9.0×10^{-4}
	284	$C_{21}H_{18}N$	284.1439	284.1443	4.0×10^{-4}
	167	$C_{13}H_{11}$	167.0861	167.0855	5.0×10^{-4}
$\left[\begin{array}{c} \phi \\ \\ C=N- \\ \\ CF_3 \end{array} \right]_2$	344	$C_{16}H_{10}N_2F_6$	344.0748	344.0723	2.5×10^{-3}
	343	$C_{16}H_9N_2F_6$	343.0670	343.0670	1.0×10^{-4}
	325	$C_{16}H_{10}N_2F_5$	325.0764	325.0794	3.0×10^{-3}
	249	$C_{14}H_{10}NF_3$	249.0765	249.0734	3.0×10^{-3}
	180	$C_{13}H_{10}N$	180.0813	180.0807	6.5×10^{-4}

APPENDIX E (Continued)

Compound	m/e	Composition	Calculated Mass	Measured Mass	Δm
	172	$C_8H_5NF_3$	172.0374	172.03670	7.0×10^{-4}
$\left[\begin{array}{c} \phi \\ \diagdown \\ C=N- \\ \diagup \\ CH_2F \end{array} \right]_2$	272	$C_{16}H_{14}N_2F_2$	272.1125	272.1134	8.8×10^{-4}
	136	C_8H_7NF	136.0562	136.0547	1.5×10^{-3}







VITA²

Dwight Wayne Miller

Candidate for the Degree of

Doctor of Philosophy

Thesis: PYROLYSIS OF AZOALKANES PART I. SECONDARY α -DEUTERIUM ISOTOPE EFFECTS. PART II. RING DEUTERIUM ISOTOPE EFFECT FOR 1,1'-DI(PHENYL-2,3,4,5,6-d₅)AZOETHANE

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