INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.

2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of “sectioning” the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.
Utz, Christopher Graham

SUBSTITUENT EFFECTS ON THE UNIMOLECULAR DECOMPOSITION OF 10-DIAZOANTHRONES

The Ohio State University

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106
PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark √.

1. Glossy photographs or pages ______
2. Colored illustrations, paper or print ______
3. Photographs with dark background ______
4. Illustrations are poor copy ______
5. Pages with black marks, not original copy ______
6. Print shows through as there is text on both sides of page ______
7. Indistinct, broken or small print on several pages √
8. Print exceeds margin requirements ______
9. Tightly bound copy with print lost in spine ______
10. Computer printout pages with indistinct print ______
11. Page(s) ______ lacking when material received, and not available from school or author.
12. Page(s) ______ seem to be missing in numbering only as text follows.
13. Two pages numbered ______. Text follows.
14. Curling and wrinkled pages ______
15. Dissertation contains pages with print at a slant, filmed as received ______
16. Other________________________________________________________

________________________________________________________

________________________________________________________

University
Microfilms
International
SUBSTITUENT EFFECTS ON THE UNIMOLECULAR DECOMPOSITION
OF 10-DIAZOANTHRONES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Christopher G. Utz, B.A.

The Ohio State University
1985

Reading Committee:
Professor Harold Shechter
Professor Jack Hine
Professor Matthew Platz

Approved by
Harold Shechter, Advisor
Department of Chemistry
Dedication

To my parents, who made it possible
To Pam, who made it probable
To Thomas, whose friendship made it attainable
To Jan, whose support, endurance, understanding, and love made it a reality
ACKNOWLEDGMENTS

I wish to express my gratitude to Professor Harold Shechter for his guidance, both on an intellectual and personal level. His influence on my life will be felt far beyond the walls of Evans Laboratory and long past the year 1985.

I would also like to thank my colleagues (and friends) for their unwavering support during some difficult times, with particular thanks to Dr. Thomas Engler and Dr. Anil Kumar for their invaluable suggestions as well as their friendship. Also, thanks are due to Lisa Frazier for all her work on the structures in this document, and to Mr. Steve Mulhall for his artistic assistance. The long hours put in by Barbara Bennett for the typing of this dissertation will be always appreciated. Finally, I wish to acknowledge the National Science Foundation and The Ohio State University for their support of this research.
VITA

February 8, 1955. .................. Born - Rochester, New York

1977. ............................... B.A., State University, College at Potsdam, New York

1977-78. ............................. University Fellow, Department of Chemistry, The Ohio State University, Columbus, Ohio

1978-79. ............................. Teaching Associate, Department of Chemistry, The Ohio State University, Columbus, Ohio

1979-82. ............................. Research Associate, Department of Chemistry, The Ohio State University, Columbus, Ohio

1983-85
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDICATION</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>VITA</td>
<td>iv</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
</tbody>
</table>

Chapter

I. STATEMENT OF THE PROBLEM.................................................................1

II. HISTORICAL..........................................................................................3
  2.1 Structural Analysis of Quinonediazides......................................4
  2.2 Reactions of Quinonediazides.....................................................7

III. KINETIC DECOMPOSITION OF DIPHENYLDIAZOMETHANES.........................27

IV. RESULTS AND DISCUSSION.....................................................................40
  4.1 Derivation of Kinetic Method.......................................................43
  4.2 Synthetic Methods.................................................................56
  4.3 Kinetic Studies.............................................................................67
V. EXPERIMENTAL ................................................................. 90
   5.1 General Techniques ...................................................... 90
   5.2 Kinetic Procedures ....................................................... 91
   5.3 Synthesis ................................................................. 93

APPENDIX .................................................................................. 110

REFERENCES ............................................................................. 121
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. N-N Stretching Frequencies in Selected Molecules</td>
<td>5</td>
</tr>
<tr>
<td>2. Bond Lengths from X-Ray Analyses of 7, 8, and 9</td>
<td>6</td>
</tr>
<tr>
<td>3. Total Relative Rate Factors for Reactions of 17 and Phenyl Radicals with Aromatic Substrates</td>
<td>11</td>
</tr>
<tr>
<td>4. Relative Rate Constants for Overall Substitution of Benzene Derivatives</td>
<td>13</td>
</tr>
<tr>
<td>5. Product Distributions for Reactions of 22 with PhX</td>
<td>13</td>
</tr>
<tr>
<td>6. Competing Reactions of 12 in Allyl Chloride in the Presence of Hexafluorobenzene</td>
<td>16</td>
</tr>
<tr>
<td>7. Photolysis of 12 in cis-2-Butene Diluted with Hexafluorobenzene</td>
<td>20</td>
</tr>
<tr>
<td>8. Photolysis of 12 in cis-2-Butene Diluted with Heavy-Atom Solvents</td>
<td>20</td>
</tr>
<tr>
<td>9. Photolysis of 3 in Hydrocarbons and in Hexafluorobenzene</td>
<td>22</td>
</tr>
</tbody>
</table>
10. Photolysis of 3 (1.25 x 10^{-2} M) in the Presence of 1.25 x 10^{-2} M Triphenylphosphine in Hydrocarbon Solvents.................................22

11. Thermal Decomposition of Diphenyldiazomethane in Benzene and Toluene at 85 °C.................................29

12. Thermal Decomposition of Diphenyldiazomethane (1) in Acetonitrile at 85 °C........................................30

13. Thermal Decomposition of Diphenyldiazomethane (1) in Aqueous Acetonitrile at 85 °C...........................31

14. Kinetic Parameters for Decomposition of Diphenyl-
    Diazomethane in 2.18 M H2O/1,2-Dimethoxyethane at 75 °C.................................................................35

15. Unimolecular Rate Coefficients and Hammett Substituent Constants for Thermolyses of Substituted Diphenyldiazomethanes in 2.18 M H2O/1,2-Dimethoxyethane at 75 °C.............................35

16. Unimolecular Rate Constants for Thermal Decomposition of 10-Diazoanthrone (3) at 97 °C in 1-Propanol.................................................................52

17. Rates of Decomposition of 9 x 10^{-5} M 10-Diazoanthrone (3) in Media of Different Compositions at 117 °C.................................................................53

18. Decompositions of Scrupulously Degassed Solutions of 3 in 1-Butanol at 110 °C..........................................56
19. Decomposition of Substituted 10-Diazoanthrones (3-Z) in 1-Butanol at 100 °C: Observed Rate Coefficients .................................................. 68

20. Average Unimolecular Rate Coefficients for the Decompositions of 2-Substituted-10-Diazoanthrones (3-Z) in 1-Butanol at 100 °C ........................................... 71

21. Rate Constants for Decompositions of 2-Substituted-10-Diazoanthrones (3-Z) in 1-Butanol at 90 °C and 106 °C .............................................................. 77

22. Average Unimolecular Rate Constants for Decomposition of 2-Substituted-10-Diazoanthrones in 1-Butanol at 90 °C and 106 °C ............................................ 77

23. Thermodynamic Parameters for Decompositions of 2-Substituted-10-Diazoanthrones in 1-Butanol Between 90 °C and 106 °C ........................................... 83

24. Total Rate Factors for Phenylation of p-Substituted Toluenes in p-Dichlorobenzene at 80 °C ................................................................. 85
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PE diagram for reaction of 23 with benzene</td>
<td>14</td>
</tr>
<tr>
<td>2.</td>
<td>Correlation of the rate coefficients for unimolecular thermal decomposition of diphenyldiazomethanes with Hammett resonance-enhanced constants</td>
<td>36</td>
</tr>
<tr>
<td>3.</td>
<td>Comparison of kinetic and ground state substituent effects in diphenyldiazomethanes</td>
<td>36</td>
</tr>
<tr>
<td>4.</td>
<td>Transition-state for loss of nitrogen from substituted diphenyldiazomethanes</td>
<td>39</td>
</tr>
<tr>
<td>5.</td>
<td>Orbital preferences</td>
<td>41</td>
</tr>
<tr>
<td>6.</td>
<td>Possible singlet carbenes generated from thermal decomposition of 3</td>
<td>48</td>
</tr>
<tr>
<td>7.</td>
<td>Depiction of graphical analysis of decompositions of 10-diazoanthrone in varied solution compositions</td>
<td>54</td>
</tr>
<tr>
<td>8.</td>
<td>Diagram of reaction cell used for decompositions of 3</td>
<td>55</td>
</tr>
</tbody>
</table>
9. Hammett plot of rate constants vs. substituent effects for decomposition of 2-substituted-10-diazoanthrones in 1-butanol at 100 °C.................................................................73

10. Yukawa-Tsuno plot of rate constants vs. separated substituent effects for the decomposition of 2-substituted-10-diazoanthrones in 1-butanol at 100 °C.................................................................75

11. Hammett plots of rate constants vs. $\sigma^+$ for decompositions of 2-substituted -10-diazaanthrones in 1-butanol at 90 °C and 106 °C..........................................................................................79

12. Yukawa-Tsuno plot for decompositions of 1-substituted-10-diazoanthrones in 1-butanol at 90 °C.................................................................................................................................81

13. Yukawa-Tsuno plot for decompositions of 2-substituted-10-diazoanthrones in 1-butanol at 106 °C.................................................................................................................................82

14. Arrhenius plot of ln k vs. 1/T for the decompositions of 2-substituted-10-diazoanthrones in 1-butanol at 106 °C.................................................................................................................................84

15. Homolytic loss of nitrogen from 3-Z to give singlet diradical 10-anthronylidene.........................................................85

16. Homolysis of the diazo moiety of 10-diazoanthrones 3-Z to give triplet 10-anthronylidene and triplet nitrogen.................................................................86
17. Possible modes for linear loss of nitrogen in the transition states for decompositions of 3-Z.................................................................87

18. Decomposition of 3-Z via non-linear extrusion of nitrogen to give \( \sigma^2 \) 10-anthronylidenes.................................................................88

19. Transition state for non-linear decomposition of substituted diphenyldiazomethanes.................................................................89

20. Graphical analysis of the thermal decomposition of 2-methyl-10-diazoanthrone at 100 °C.................................................................112

21. Graphical analysis of the thermal decomposition of 2-methoxy-10-diazoanthrone at 100 °C.................................................................114

22. Graphical analysis of the thermal decomposition of 2-chloro-10-diazoanthrone at 100 °C.................................................................116

23. Graphical analysis of the thermal decomposition of methyl 10-diazoanthrone-2-carboxylate at 100 °C.................................118

24. Graphical analysis for the thermal decomposition of 10-diazoanthrone at 100 °C.................................................................120
Chapter I

STATEMENT OF THE PROBLEM

Thermal decompositions of diphenyldiazomethanes (1) reveal that all electron-donating and electron-withdrawing para-substituents increase the rate of formation of diphenylmethylenes (1a):

A mechanism which explains these observations involves simultaneous overlap of the π-systems of both aromatic rings with the sp³ orbitals at the methylene center in the transition state (Eq. 1). This stabilization requires the phenyl rings to be twisted out of coplanarity.
The present study investigates the kinetic thermolytic behavior of the rigid phenylenic diazo compounds 9-diazofluorene (2) and 10-diazoanthrone (3), and their varied para-substituted derivatives.

The purposes of this research are to 1) thermolyze para-substituted rigid diazo compounds 2 and 3 and measure their rates of decomposition and 2) determine the natures of the transition states and the mechanistic features of such decomposition reactions. The above objectives require development of a suitable kinetic method for following decomposition of thermally stable but highly oxygen-sensitive diazo compounds.
Diazo oxides or quinonediazides are multi-behavioral organic compounds which have commercial utility in the photographic and dye industries and in the production of explosives.

3,5-Dinitrobenzene-1,2-diazooxide (1), the first aromatic diazo oxide to be synthesized, was obtained from picramic acid and dinitrogen trioxide (Eq. 1).\textsuperscript{1}

\[
\begin{align*}
\text{OH} & \\
\text{O}_2\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{O}_2\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\ (1)
\end{align*}
\]

A series of parent quinonediazides have been prepared over the years, beginning with 1,2- and 2,1-naphthoquinonediazides in 1894,\textsuperscript{2} 1,2-benzoquinonediazide (2) in 1896,\textsuperscript{3} 1,4-benzoquinonediazides in 1945,\textsuperscript{4} and 9,10-phenanthraquinonediazide in 1957.\textsuperscript{5} 9,10-Anthaquinonediazide (3) was reported in 1964.\textsuperscript{6,7}

Quinonediazides are hybrid structures; thus 2a and 3a are important resonance contributors to 2 and 3, respectively, and the dipolar representations rationalize many aspects of the chemistry of such molecules.
2.1 STRUCTURAL ANALYSIS OF QUINONEDIAZIDES

That the structures of quinonediazides are best represented as resonance hybrids is borne out by their physical properties, in particular their infrared spectra, dipole moments, and X-ray structures.

The stretching frequencies for the C-O and the N-N bonds in quinonediazides fall between 1600-1650 cm$^{-1}$ and 2000-2250 cm$^{-1}$, respectively. The C-O values are between that of a ketone (1720 cm$^{-1}$) and an enol (1550-1600 cm$^{-1}$), and the N-N values are between those of molecular nitrogen (2330 cm$^{-1}$) and the C=N=N stretch in diazoalkanes. Indeed, the effect of conjugative interaction of diazo and carbonyl groups in quinonediazides is illustrated in Table 1. The absorption for N-N stretching in 1,4-benzoquinonediazide (5) is between that in diazonium salt 6 and diazocyclohexadiene 4.
Table 1

N-N Stretching Frequencies in Selected Molecules

<table>
<thead>
<tr>
<th>Compound</th>
<th>CN (cm(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Compound 4" /></td>
<td>2049</td>
<td>9</td>
</tr>
<tr>
<td><img src="image" alt="Compound 5" /></td>
<td>2133</td>
<td>10</td>
</tr>
<tr>
<td><img src="image" alt="Compound 6" /></td>
<td>2236</td>
<td>11</td>
</tr>
</tbody>
</table>

Dipole moments provide further evidence for the hybrid structures of quinonediazides. Using values of \(\mu_{CN} = 1.4\) D for diphenyldiazomethane\(^{12}\) and \(\mu_{CO} = 4.17\) D for tropone\(^{13}\), 2.8 D is computed for the dipole moment of 5. Calculations for 5 as the diazonium phenolate estimate a dipole moment of 27 D.\(^{14}\) Actual measurement of the moment of 1,4-benzoquinonediazide (5) gives a value of 5.0 D,\(^{15}\) larger than calculated as a diazo ketone, but far less than that of the totally zwitterionic form, suggesting an intermediate hybrid structure.

X-ray diffraction analysis has been performed on 2,6-dichloro-1,4-benzoquinonediazide (7).\(^{16}\) Comparison of the bond lengths in 7 with those of 2,6-dichloro-1,4-benzoquinone (8)\(^{17}\) and benzenediazonium chloride (9)\(^{18}\) gives further insight into the structures of quinonediazides (Table 2).
Table 2

Bond Lengths from X-Ray Analyses of 7,16 8,17
and, 918

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>C(_1)-O</td>
<td>1.221</td>
</tr>
<tr>
<td>C(_1)-C(_2)</td>
<td>1.461</td>
</tr>
<tr>
<td>C(_2)-C(_3)</td>
<td>1.368</td>
</tr>
<tr>
<td>C(_3)-C(_4)</td>
<td>1.393</td>
</tr>
<tr>
<td>C(_4)-N</td>
<td>1.368</td>
</tr>
<tr>
<td>N-N</td>
<td>1.099</td>
</tr>
<tr>
<td>C(_4)-C(_5)</td>
<td>1.401</td>
</tr>
<tr>
<td>C(_5)-C(_6)</td>
<td>1.360</td>
</tr>
<tr>
<td>C(_6)-C(_1)</td>
<td>1.434</td>
</tr>
</tbody>
</table>

Once again, experiments indicate that the actual structure of a quinonediazide is something between its benzenoid and quinoid forms. The C\(_2\)-C\(_3\) and C\(_5\)-C\(_6\) bond lengths in 7 are longer than in 8, showing less double bond character than in quinone 8, but not as long as in diazonium salt 9.

While the carbonyl bond lengths in quinonediazide 7 and quinone 8 are virtually identical, the N-N bond lengths in 7 and in diazonium salt 9 are equal to that in molecular nitrogen.19 In comparison with the C-N bond lengths of 1.313 Å in bis-1,4- diazo-2,3-butanedione,20
the \( C_4-N \) bond in 7 has less double bond character. Thus the quinone-diazide appears to have simultaneous diazo, carbonyl, and diazo oxide characteristics.

Table 2 shows further that the \( C_1-C_2 \) and \( C_1-C_6 \) bond lengths in 7 are closer to those of quinone 8, whereas the lengths of \( C_3-C_4 \) and \( C_4-C_5 \) are closer to those of diazonium salt 9. This leaves a further impression of a molecule of "split character", offering the opportunity to react as either a diazonium salt or a diazo compound.

Physical data thus reveal the hybrid character of quinone-diazides. This character is further illustrated by reactions of quinonediazides which give products with extrusion and with retention of nitrogen.

### 2.2 REACTIONS OF QUINONEDIAZIDES

Reaction conditions dictate the course of reactions of quinone-diazides. Given a source of energy such as heat or ultraviolet light, the title compounds will lose nitrogen and carbenes will be the resulting intermediates. When treated with nucleophiles in neutral and alkaline media, reactions as quinonediazides occur.

9,10-Anthraquinonediazide (or 10-diazoanthrone, 3) reacts with p-benzoquinone (Eq. 2), dimethyl acetylenedicarboxylate (Eq. 3), and benzyne (Eq. 4) to give spiropyrazoles.6
Formation of 11 is believed to occur via enolization of aduct 10. Triphenylphosphine also adds to 3 to form 9,10-anthraquinone-10-triphenylphosphazene.

2,6-Di-t-butyl-1,4-benzoquinonediazide (12) reacts with various nucleophiles.\textsuperscript{21,22} Primary and secondary amines add to 12 to form triazenes (Eq. 5) which are transformed further depending upon the amine.\textsuperscript{21}

Treatment of 12 with secondary amines leads to 3,3-dialkyl-1-(4'-hydroxy-3',5'-di-t-butylphenyl)triazenes 13 in good yields (85-95%). However, 13 is not isolated in the reactions with primary amines. 2,6-Di-t-butylphenol (14), 2,6-di-t-butylbenzoquinone (15) and
3,3',5,5'-tetra-t-butyldiphenoquinone (16) are found. Reduction products 15 and 16 are believed to arise via decomposition of the initial triazenes as shown in Scheme I.

Finally, 12 does not react with aniline, whereas addition does occur with 5, a more electrophilic 1,4-benzoquinone diazide. The
preparative results are consistent with the following stability order for the possible triazenes formed:

\[ \text{Ar-N=N-NHAr} > \text{Ar-N=N-NR}_2 > \text{Ar-N=N-NHR} \]

Isolation of triazenes is thus easier from aniline and secondary amines than from primary amines. Hence, the structure and nucleophilicity of the amine, reaction conditions, and electrophilicity of the quinonediazide are critical for efficient synthesis of the corresponding triazenes.

Generation of carbenes from 1,4-quinonediazides has been studied by several researchers. For example, thermolysis of 3,5-dihalo-1,4-benzoquinonediazides has been investigated in aromatic solvents.\(^{26,27}\) It was initially argued that reactions of 3,5-dibromo-1,4-benzoquinonediazide (17) with varied benzenes to give biphenyl derivatives proceed by the following mechanism (Eq. 6).

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{N}_2 & \quad \triangle \\
\text{Ar} \quad \text{Br} & \quad \text{Br} \\
\text{17} & \quad \text{18} \\
\end{align*}
\]

(6)

\[
\begin{align*}
\text{Br} & \quad \\
\text{O} & \quad \text{Br} \\
\text{Z} & \quad \text{H} \\
\text{19} & \quad \text{20} \\
\end{align*}
\]

The major products of each reaction are dependent upon the substituted benzene (C\(_6\)H\(_5\)-Z) and the experimental conditions. When Z = Br, Cl, or
NO₂, polymeric products predominate. When Z = H, F, OCH₃, N(CH₃)₂, or CN, 20 was isolated in fair yield. Formation of 20 becomes the major path upon addition of 1% ethanol to the reaction mixture.

Since the mechanism proposed involved rate-determining formation of aryl radicals 19, it was hypothesized that the relative rates of carbenic attack on the substituted benzenes would be comparable to those of phenyl radicals.²⁸ Table 3 shows that, in the two systems, the spread of rates is small, as would be expected for radical attack on benzenoid substrates.

Table 3

<table>
<thead>
<tr>
<th>Z in C₆H₅-Z</th>
<th>k₁₇</th>
<th>kₚₘₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMe₂</td>
<td>2.8</td>
<td>---</td>
</tr>
<tr>
<td>Pyridine</td>
<td>2.6</td>
<td>1.04</td>
</tr>
<tr>
<td>OMe</td>
<td>1.6</td>
<td>2.5</td>
</tr>
<tr>
<td>F</td>
<td>0.46</td>
<td>1.35</td>
</tr>
<tr>
<td>CO₂Me</td>
<td>0.78</td>
<td>---</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.54</td>
<td>1.44</td>
</tr>
<tr>
<td>o-Cl₂</td>
<td>0.28</td>
<td>---</td>
</tr>
<tr>
<td>H</td>
<td>1.0</td>
<td>1.00</td>
</tr>
</tbody>
</table>

While the products 20 were isolated in all instances, distribution of isomers was only determined in the reactions of 17 and chlorobenzene.²⁶ The latter product mixture contained 60% ortho- and 40% para- substituted 4'-hydroxydiphenyls, thus showing very selective electrophilic behavior. The orientation in substitution was thus presumed to result from polarization of the π-electrons in the carbene 18, a structure approximating 21.
In order to understand the substitution mechanism better, the product distribution from reactions of 3,5-dichloro-1,4-benzoquinonediazide (22) with various benzenes was investigated. The relative rates of reaction with a benzene as well as the isomer distribution of the substitution products were also determined (Tables 4 and 5).

Comparison of the relative rate constants for aromatic substitution by 22 with those for substitution by the phenyl radical and for nitration by nitric acid in acetic anhydride reveals some similarity to electrophilic substitution, though demonstrating a lack of substrate selectivity (PhX/PhY). Additionally, the strong positional selectivity exhibited is definitely indicative of electrophilic aromatic substitution by 22 and seemingly rules out a radical mechanism.

The results with 22 were explained by three intermediates (23-26), in which 23-24 is in rapid equilibrium with singlet diradical 25.
The polymerization observed with halobenzenes is believed to be a result of crossover to triplet diradical 26 enhanced by the presence of heavy atoms in the solvent. The ethanol added (1%) is presumed to hydrogen bond with singlet carbene 23-24, retarding its conversion to 25 and/or 26, thus inhibiting polymerization and promoting electrophilic substitution.

<table>
<thead>
<tr>
<th>X in C₆H₅X</th>
<th>22</th>
<th>HNO₃/Ac₂O</th>
<th>Ph·</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>F</td>
<td>0.388</td>
<td>0.15</td>
<td>1.35</td>
</tr>
<tr>
<td>Cl</td>
<td>0.429</td>
<td>0.033</td>
<td>1.44</td>
</tr>
<tr>
<td>Br</td>
<td>0.345</td>
<td>0.03</td>
<td>1.75</td>
</tr>
<tr>
<td>OMe</td>
<td>1.276</td>
<td>---</td>
<td>2.5</td>
</tr>
<tr>
<td>CO₂Me</td>
<td>0.522</td>
<td>0.0037</td>
<td>---</td>
</tr>
<tr>
<td>CN</td>
<td>0.355</td>
<td>---</td>
<td>3.6</td>
</tr>
</tbody>
</table>

| X in PhX | Proportions of Products (%) |
|---|---|---|
| o- | m- | p- |
| H | 62.1 | 0 | 37.8 |
| Cl | 62.0 | 0 | 32.0 |
| Br | 42.3 | 0 | 31.6 |
| OMe | 72.8 | 0 | 27.2 |
| CO₂Me | 35.1 | 47.2 | 17.7 |
| CN | 45.0 | 16.5 | 38.5 |

a 26% ipso-substitution occurs.
The mechanism of substitution is outlined in Eq. 7.

\[
\begin{align*}
23 \rightarrow 27 \rightarrow 28 \rightarrow 29
\end{align*}
\]

Assuming \( k_1 \) to be rate-determining, highly exothermic and of low activation energy allows explanation of the low substrate selectivity and the very high positional selectivity (Fig. 1).

If formation of 27 has a low activation energy, little effect is expected from a change in \( Z \). Each of the three possible intermediates 27 will open to form the more stable of two dipolar species 28, thus leading to highly selective electrophilic substitution patterns.

**Figure 1:** PE diagram for reaction of 23 with benzene: rate of isomerization of 27 slower than final proton transfer from 28.
Thermolyses and photolyses of substituted 1,4-quinonediazides have been conducted. In attempts to determine the multiplicities of the reactive forms of the carbenes from 2,6-dialkyl- or diaryl-1,4-benzoquinonediazides, the stereochemistry of addition to olefins was investigated. For example, 2,6-di-t-butyl benzoquinonediazide (12) was thermolyzed and photolyzed in trans-2-butene (Eq. 8) and in allyl chloride.

![Chemical structure](image)

Addition to trans-2-butene is stereospecific to give trans-cyclopropane (30), even in the presence of varied concentrations of hexafluorobenzene diluent (up to 90.3 mole %) to enhance singlet-triplet inversion, demonstrating that the rate of singlet reaction with the medium exceeds the rate of inversion.

This finding was further corroborated in studies with allyl chloride, in which singlet 12s inserts into the C-Cl bond, while triplet 12t adds to the double bond (Eq. 9).
Once again, the medium was diluted with hexafluorobenzene to enhance triplet formation. In decomposition of 12 in allyl chloride, there is no significant effect (Table 6) on the ratio of cyclopropane 32 to insertion product 31 obtained above -130 °C (the glass transition of allyl chloride). Photolysis in matrix, however, does show a marked temperature effect.

Table 6

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>HFB%</th>
<th>Yield(%)</th>
<th>32/31</th>
</tr>
</thead>
<tbody>
<tr>
<td>95 °C</td>
<td></td>
<td>31</td>
<td>32</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>36.1</td>
<td>40.8</td>
</tr>
<tr>
<td>32.2</td>
<td>37.1</td>
<td>39.3</td>
<td>0.6</td>
</tr>
<tr>
<td>58.1</td>
<td>38.9</td>
<td>46.7</td>
<td>1.0</td>
</tr>
<tr>
<td>77.5</td>
<td>28.3</td>
<td>36.3</td>
<td>2.4</td>
</tr>
<tr>
<td>94.0</td>
<td>32.2</td>
<td>37.8</td>
<td>3.7</td>
</tr>
<tr>
<td>hv, 20 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 °C</td>
<td>92.8</td>
<td>37.2</td>
<td>47.1</td>
</tr>
<tr>
<td>0 °C</td>
<td>93.7</td>
<td>35.2</td>
<td>40.9</td>
</tr>
<tr>
<td>-68 °C</td>
<td>93.7</td>
<td>40.3</td>
<td>37.8</td>
</tr>
<tr>
<td>-130 °C</td>
<td>0</td>
<td>35.7</td>
<td>34.0</td>
</tr>
<tr>
<td>-160 °C</td>
<td>0</td>
<td>17.8</td>
<td>34.0</td>
</tr>
<tr>
<td>-195 °C</td>
<td>0</td>
<td>5.5</td>
<td>69.8</td>
</tr>
</tbody>
</table>
From these results, the authors offer several conclusions:

1. Addition of singlet 3,5-di-t-butyl-4-ketocyclohexadienylidene proceeds at about the same rate as that of the triplet.

2. The dilution method is ineffective for studying the specific behaviors of \textit{12s} and \textit{12t} since the rate of substrate reaction exceeds that of inversion, even at low temperatures.

3. At lower temperatures in matrix, the rate of insertion of \textit{12} into a C-Cl bond becomes equal to that of singlet-triplet inversion.\textsuperscript{34}

The reactions of 1,4-quinonediazides in alcohols and carboxylic acids\textsuperscript{31} and in ketones\textsuperscript{32} have been studied. Thermolysis of \textit{12}, \textit{33}, and \textit{5} in alcohols and carboxylic acids gives the corresponding hydroquinone ethers and esters, respectively, in good yields (Eq. 10).

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{R} & \quad \text{R} \\
\text{N}_2 & \\
\Delta \quad \text{-N}_2 \\
\text{R'} & \quad \text{OH} \\
\text{R} & \quad \text{OR'} \\
\end{align*}
\]

\textsuperscript{(10)}

\textit{12} \hspace{1cm} \text{R = t-Bu} \hspace{1cm} \text{R' = alkyl, acyl, C}_6\text{H}_5

\textit{33} \hspace{1cm} \text{R = i-Pr}

\textit{5} \hspace{1cm} \text{R = H}

Products from thermolyses of \textit{12} in ketones (acetone, di-n-propyl ketone, cyclohexanone, and acetophenone) depend upon the carbonyl compound used. Epoxyspiranes \textit{34} are obtained from reaction with
dialkyl ketones in good yields and are believed to form via oxonium ylids (Eq. 11).

\[
\begin{align*}
\text{R}_1 = & \text{R}_2 = \text{CH}_3 \\
\text{R}_1 = & \text{R}_2 = \text{n-Pr} \\
\text{R}_1 = & \text{R}_2 = -(\text{CH}_2)_5- \\
\end{align*}
\]

Epoxyspiranes are not isolated, however, from 12 and acetophenone; only phenols 35 and 36 are obtained (Eq. 12). While the mechanism for the formation of the \( p \)-substituted product is not clear, oxonium ylid 37 has been proposed as a possible intermediate for the process. Ketone 36 is thought to be the result of insertion into the methyl group of acetophenone.

Decomposition of 12 in various organic halides has demonstrated the involvement of intermediate ylids. Photolysis of 12 in
cis-2-butene diluted with alkyl halides has been described and it is suggested that halonium ylids are reaction intermediates and that the stereochemical effect is not a result of intersystem crossing caused by heavy atoms.

Addition of hexafluorobenzene to cis-2-butene (Table 7) lowers the stereospecificity of cyclopropane formation, and 3,3',5,5'-tetra-t-butyl-diphenoquinone (16) is not observed. Such results are expected from the triplet carbene 12t.

However, dilutions with alkyl bromides and iodides produce large yields of diphenoquinone 16 (Table 8). Further, addition to cis-2-butene is stereoselective. Clearly, these are not the results of singlet-triplet inversion as in the presence of hexafluorobenzene. The authors propose that halonium ylids 38 are intermediates in the production of 16 (Eq. 13). Isolation of bromonium bromide 39 from photolysis of 12 in 4-bromo-2,6-diisopropylphenol lends credence to this hypothesis.

\[
\begin{align*}
\text{HO} & \quad \text{Br}^+ \\
\text{Br}^- & \quad \text{OH}
\end{align*}
\]

39

The chemistry of 9,10-anthraquinonediazide (10-diazoanthrone, 3) has been studied by several investigators. Photolyses and thermolyses of 3 have been conducted in hydrocarbon solvents and with pyridine N-oxide. Additions of 3 to electron-poor olefins have also been investigated. Photolysis of 3 in benzene, toluene, cyclohexane, and cyclohexene leads to products of triplet reactions
### Table 7

**Photolysis of 12 in cis-2-Butene Diluted with Hexafluorobenzene**

<table>
<thead>
<tr>
<th>Mole % C₆F₆</th>
<th>Total cyclopropane yield (%) c:t</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>74</td>
<td>85</td>
</tr>
<tr>
<td>90</td>
<td>77</td>
</tr>
</tbody>
</table>

### Table 8

**Photolysis of 12 in cis-2-Butene Diluted with Heavy-Atom Solvents**

<table>
<thead>
<tr>
<th>Diluent</th>
<th>Mole % diluent</th>
<th>(c/t)</th>
<th>16/(c+t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-C₃H₇Br</td>
<td>47</td>
<td>3.4</td>
<td>0.8</td>
</tr>
<tr>
<td>CH₃I</td>
<td>57</td>
<td>all c</td>
<td>2.3</td>
</tr>
<tr>
<td>C₂H₅I</td>
<td>44</td>
<td>all c</td>
<td>1.4</td>
</tr>
<tr>
<td>C₂H₅Br</td>
<td>42</td>
<td>5.4</td>
<td>0.2</td>
</tr>
<tr>
<td>CF₃I</td>
<td>47</td>
<td>all c</td>
<td>1.2</td>
</tr>
</tbody>
</table>
(Eq. 14). Insertion products 41 are minor (10%). Also, addition of 3 to cyclohexene to form a cyclopropane does not occur - only insertion into allylic hydrogen takes place. These findings were explained via abstraction of hydrogen from the medium by triplet 10-anthronylidene (3t) to create radical pairs.

\[
\text{hv, RH} \rightarrow \text{R-R} + \text{R} - \text{R}^+ \quad (14)
\]

Addition of pyridine N-oxide to benzene solutions of 3 causes a decrease in the yields of radical products 40 and 41. Anthraquinone results from deoxygenation of the N-oxide by 10-anthronylidene. In a cyclohexene solution of 3 and pyridine-N-oxide, however, the radical process is strongly favored.

Increasing the concentration of 3 and choosing media less prone to hydrogen abstraction by 10-anthronylidene yields the results in Table 9. In all systems having an abstractable hydrogen, azine 42 is not formed (Eq. 15).

\[
3 \xrightarrow{\text{hv, RH}} 40 + 41 + R - R^+ \quad (15)
\]
Table 9

**Photolysis of 3 in Hydrocarbons and in Hexafluorobenzene**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$10^2<a href="M">3</a>$</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>$C_6H_6$</td>
<td>3.3</td>
<td>8</td>
</tr>
<tr>
<td>$C_6H_5CH_3$</td>
<td>3.3</td>
<td>0</td>
</tr>
<tr>
<td>$C_6H_{10}$</td>
<td>1.25</td>
<td>0</td>
</tr>
<tr>
<td>$C_6H_{12}$</td>
<td>1.25</td>
<td>0</td>
</tr>
<tr>
<td>$C_6F_6$</td>
<td>3.3</td>
<td>33</td>
</tr>
</tbody>
</table>

As is seen in Table 10, with equivalent amounts of 3 and triphenylphosphine, addition of cyclohexene significantly lowers the yield of 9,10-anthronylidenephosphorane (43), while the yield of radical combination products 40 and 41 increases dramatically.

![Diagram](image)

Table 10

**Photolysis of 3 (1.25 x 10^{-2} M) in the Presence of 1.25 x 10^{-2} M Triphenylphosphine in Hydrocarbon Solvents**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>43(%)</th>
<th>(40 + 41)(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_6$</td>
<td>75</td>
<td>19</td>
</tr>
<tr>
<td>3.75 x 10^{-2} M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_6H_{10}/C_6H_6$</td>
<td>42</td>
<td>48</td>
</tr>
<tr>
<td>11.25 x 10^{-2} M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_6H_{10}/C_6H_6$</td>
<td>0</td>
<td>80</td>
</tr>
</tbody>
</table>
All of these results are explained from the singlet-triplet equilibrium for 10-anthronylidene as illustrated in Scheme II, strongly favored in the triplet direction.39

Scheme II

\[
\begin{align*}
o_D & \xrightarrow{h\nu} 1_D^* \xrightarrow{ISC} 3_D^* \\
42 \text{ or } 43 + \text{Nu:} & \xrightarrow{1_A} 3_A \xrightarrow{RH} A-H + R^* \xrightarrow{} 40 + 41 + R-R
\end{align*}
\]

D = 10-Diazoanthrone
A = Anthronylidene

In the presence of a nucleophile which reacts strongly with a singlet carbene, the equilibrium is shifted, thus forming more singlet (\(1_A\)) and allowing greater singlet reaction. In the presence of only a small quantity of a labile hydrogen source, however, the more stable triplet (\(3_A\)) predominates and products of radical processes are observed.

Syntheses of cyclopropanes via thermolysis of 3 are reported.6 Additions to acrylonitrile (65%), methyl vinyl ketone (61%), trans-dibenzylethylene (91%), and p-benzoquinone (37%) were carried out in good yield and stereospecifically to afford cyclopropanes (Eq. 16).
When 3 is heated in benzene with diethyl azodicarboxylate, an unusual process occurs in that hydrazone 44 is formed, believed to be produced via Eq. 17.

\[
\begin{align*}
3 + \text{NN} \quad \xrightarrow{\Delta} \quad \text{N(N(CO_2Et)_2}
\end{align*}
\]

Thermolyses of 3 have also been conducted in maleic anhydride, and N-phenylmaleimide to give cyclopropanes. In the reactions of diethyl fumarate and diethyl maleate, however, the mechanisms involved do not appear to be identical, as might be expected (Eq. 18).
The latter results (Eq. 18) were interpreted to indicate concerted 1,3-dipolar addition as opposed to a stepwise mechanism, since a common zwitterion would lead to the same product in each case. The initial reaction, then, is formation of 1-pyrazoline 47 which can (a) lose nitrogen or (b) isomerize to a 2-pyrazoline, leading to 45 and 46, respectively. Scheme III summarizes the possibilities in light of the given data.
It can be argued that steric strain accelerates isomerization of 47c to 46 by decreasing the interaction between the two ethoxycarbonyl groups, whereas 47t would not gain that same stabilization. The longer lifetime of the trans-1-pyrazoline allows greater opportunity, then, for extrusion of nitrogen and formation of cyclopropane 45.
Chapter III

KINETIC DECOMPOSITIONS OF DIPHENYLDIAZOMETHANES

Thermal decomposition of diphenyldiazomethane (1) has been extensively investigated in varied solvents (SH). Early kinetic studies\(^4\) showed the decomposition (Eq. 1) to be first-order in diazo compound which undergoes rate-determining loss of nitrogen to produce diphenylmethylenes (1a):

\[
\begin{align*}
\text{Ph}_2\text{CN}_2 & \xrightarrow{k_1} \text{Ph}_2\text{C} : \\
\text{Ph}_2\text{C} : & \xrightarrow{k_2} \text{Ph}_2\text{C} = \text{N} = \text{N} = \text{CPh}_2 + 4 + 5 \\
\text{Ph}_2\text{C} : & \xrightarrow{k_3} \text{Ph}_2\text{CSH} \\
\end{align*}
\]

Bethell and co-workers\(^4\) measured the rates of thermolysis of 1 in benzene, toluene, acetonitrile, and in mixtures of acetonitrile with ethanol and with water. Utilization of the steady-state approximation allows extraction of unimolecular rate constants \(k_1\) from the observed rates of decomposition, \(k_{\text{obs}}\), as follows:

The rate of decomposition of diphenyldiazomethane (1) is the sum of its unimolecular and bimolecular rates:

\[
\frac{-d[\text{Ph}_2\text{CN}_2]}{dt} = k_1[\text{Ph}_2\text{CN}_2] + k_2[\text{Ph}_2\text{C} :][\text{Ph}_2\text{CN}_2] \quad (2)
\]

Steady-state treatment of \((\text{Ph}_2\text{C} :)\) yields
\[
\frac{d[\text{Ph\textsubscript{2}C::}]}{dt} = k_1[\text{Ph\textsubscript{2}CN\textsubscript{2}}] - k_2[\text{Ph\textsubscript{2}C::}][\text{Ph\textsubscript{2}CN\textsubscript{2}}] - k_3[\text{Ph\textsubscript{2}C::}][\text{SH}] \quad (3)
\]

and

\[
[\text{Ph\textsubscript{2}C::}] = \frac{k_1[\text{Ph\textsubscript{2}CN\textsubscript{2}}]}{k_2[\text{Ph\textsubscript{2}CN\textsubscript{2}}] + k_3[\text{SH}]} \quad (4)
\]

Assuming that \((\text{SH})\) is constant throughout the reaction, substitution of Eq. 4 into Eq. 2 gives

\[
\frac{-d[\text{Ph\textsubscript{2}CN\textsubscript{2}}]}{dt} = k_1[\text{Ph\textsubscript{2}CN\textsubscript{2}}] + \frac{k_2[\text{Ph\textsubscript{2}CN\textsubscript{2}}]}{k_2[\text{Ph\textsubscript{2}CN\textsubscript{2}}] + k_3[\text{SH}]} \quad (5)
\]

and multiple integration by parts between limits yields the kinetic expression

\[
-k_1 t = \ln \left( \frac{[\text{Ph\textsubscript{2}CN\textsubscript{2}}]}{[\text{Ph\textsubscript{2}CN\textsubscript{2}}]_0} \right) = \ln \left( \frac{2(k_2/k_3)[\text{Ph\textsubscript{2}CN\textsubscript{2}}]_0/[\text{SH}] + 1}{2(k_2/k_3)[\text{Ph\textsubscript{2}CN\textsubscript{2}}]/[\text{SH}] + 1} \right) \quad (6)
\]

The ratio \(k_2/k_3\) represents the relative rates of formation of products resulting from second-order processes, benzophenone azine (2), tetra-phenylethylene (4), and benzophenone (5), and of capture by the solvent. Values of \(k_2/k_3\) were rigorously computed from the yields of azine.
Calculation of $k_2/k_3$ allows for determination of $k_1$. As is illustrated in Table 11, values of $k_1$ are not significantly different for decompositions in benzene and toluene, while disparate yields of azine 2 and thus the values of $k_2/k_3$, demonstrate a marked effect of the medium upon product distribution. Thus, reaction with the solvent competes effectively with azine (2) formation when insertion into a weak bond in the solvent is possible.

Table 11

<table>
<thead>
<tr>
<th>Solvent</th>
<th><a href="M">1</a></th>
<th>$10^2k_{obs}$ (min$^{-1}$)</th>
<th>$10^2k_1$ (min$^{-1}$)</th>
<th>2(%)</th>
<th>$k_2/k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.0538</td>
<td>0.96</td>
<td>0.55</td>
<td>61.5</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>0.0182</td>
<td>0.78</td>
<td>0.66</td>
<td>36.5</td>
<td>37</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.0504</td>
<td>0.54</td>
<td>0.49</td>
<td>10.6</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>0.0252</td>
<td>0.58</td>
<td>0.51</td>
<td>6.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Thermolysis of 1 in acetonitrile gives slightly enhanced rate coefficients relative to those in benzene and toluene. The results are believed to arise from a medium effect (Table 12). That the values of $k_1$ are constant and independent of the yield of azine 2 argues against any large contribution of a second-order reaction in diazo compound 1, i.e. $k'(\text{Ph}_2\text{CN}_2)^2$. 
Table 12

Thermal Decomposition of Diphenyldiazomethane (1)
in Acetonitrile at 85 °C. 43

<table>
<thead>
<tr>
<th><a href="M">1</a></th>
<th>$10^2 k_{obs}$ (min$^{-1}$)</th>
<th>$10^2 k_1$ (min$^{-1}$)</th>
<th>2(%)</th>
<th>$k_2/k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1187</td>
<td>1.09</td>
<td>0.83</td>
<td>38.7</td>
<td>6.3</td>
</tr>
<tr>
<td>0.0668</td>
<td>0.97</td>
<td>0.75</td>
<td>24.9</td>
<td>5.5</td>
</tr>
<tr>
<td>0.0533</td>
<td>1.04</td>
<td>0.93</td>
<td>19.7</td>
<td>5.0</td>
</tr>
<tr>
<td>0.0297</td>
<td>0.94</td>
<td>0.84</td>
<td>14.9</td>
<td>6.2</td>
</tr>
<tr>
<td>0.0148</td>
<td>0.96</td>
<td>0.95</td>
<td>7.0</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Not all of the products from decomposition in acetonitrile could be identified, leaving values of $k_2/k_3$ tentative at best. Great simplification of the product mixtures results, however, upon addition of a strong carbenophile such as water. In aqueous acetonitrile, the products of decomposition of 1 are only benzophenone (5) and benz-hydrol (3, Eq. 1, S=OH), and first-order rate coefficients can be calculated via Eq. 7, a modified version of Eq. 6.

$$ -k_1t = \ln \frac{[\text{Ph}_2\text{CN}_2]}{[\text{Ph}_2\text{CN}_2]_0} \left\{ \frac{2(k_2/k_3)[\text{Ph}_2\text{CN}_2]_0/[\text{H}_2\text{O}] + 1}{2(k_2/k_3)[\text{Ph}_2\text{CN}_2]/[\text{H}_2\text{O}] + 1} \right\}^{1/2} \quad (7) $$

Evaluation of $k_2/k_3$ shows that, in all cases studied (Table 13), $(k_2/k_3)/(\text{H}_2\text{O})$ never exceeds unity. With $(\text{Ph}_2\text{CN}_2)_0$ always less than 0.13 M, the square root term in Eq. 6 in the first two half-lives never exceeds 10%, thus leaving $k_{obs}$ essentially equivalent to $k_1$. 
### Table 13

**Thermal Decomposition of Diphenyldiazomethane (1) in Aqueous Acetonitrile at 85 °C.**

<table>
<thead>
<tr>
<th><a href="M">1</a></th>
<th><a href="M">H₂O</a></th>
<th>10²k&lt;sub&gt;obs&lt;/sub&gt; (min⁻¹)</th>
<th>2 (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0668</td>
<td>----</td>
<td>0.97</td>
<td>24.9</td>
</tr>
<tr>
<td>0.0668</td>
<td>0.665</td>
<td>0.794</td>
<td>3.8</td>
</tr>
<tr>
<td>0.0668</td>
<td>0.674 D₂O</td>
<td>0.75</td>
<td>3.4</td>
</tr>
<tr>
<td>0.0668</td>
<td>1.02</td>
<td>0.76</td>
<td>4.5</td>
</tr>
<tr>
<td>0.0668</td>
<td>1.05 D₂O</td>
<td>0.70</td>
<td>4.2</td>
</tr>
<tr>
<td>0.0507</td>
<td>10.15 D₂O</td>
<td>1.40</td>
<td>?</td>
</tr>
<tr>
<td>0.0507</td>
<td>10.32</td>
<td>1.55</td>
<td>3.9&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.1187</td>
<td>----</td>
<td>1.09</td>
<td>38.7</td>
</tr>
<tr>
<td>0.1086</td>
<td>0.429</td>
<td>0.93</td>
<td>11.9</td>
</tr>
<tr>
<td>0.1262</td>
<td>0.658</td>
<td>0.76</td>
<td>3.6</td>
</tr>
<tr>
<td>0.1262</td>
<td>2.16</td>
<td>0.84</td>
<td>3.0</td>
</tr>
<tr>
<td>0.1262</td>
<td>2.16 D₂O</td>
<td>0.79</td>
<td>2.8</td>
</tr>
<tr>
<td>0.1262</td>
<td>4.07</td>
<td>1.07</td>
<td>3.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> Combined yield of azine 2 and ethylene 4

Examination of the rate constants as a function of water concentration demonstrates that there is no direct reaction of diphenyldiazomethane (1) with water. In fact, the observed rate decreases over the range of concentrations between which the yield of benzhydrol increases from 0 to greater than 90%. The slight rate increases with water concentrations greater than 10 M are believed to result from a small amount of direct hydration of diphenyldiazomethane (1).

The evidence definitively supports the mechanism outlined in Eq. 1. Thus, thermal decomposition of diphenyldiazomethane in aqueous acetonitrile proceeds with rate-determining formation of diphenylmethene (1a) which is then partitioned by the media to give the observed products.
Miller has examined the effects of **para-substitution** on the unimolecular decomposition of diphenyldiazomethanes (1-Z) using the techniques described by Bethell. The diazo compounds were decomposed in 2.18 M water/glyme (1,2-dimethoxyethane) solutions which had been thoroughly deoxygenated.

Thus, the chances for second-order loss of the diazo compounds (Eq. 8) by conversions to benzophenone azines (2), tetraphenylethlenes (4), and benzophenones (5, Scheme I) were minimized.

**Scheme I**

\[ \text{Ph}_2\text{CN}_2 \xrightarrow{\Delta} \text{Ph}_2\text{C} \xrightarrow{\text{O}_2} \text{Ph}_2\text{C} = \text{O} - \text{O} \]

\[ \text{Ph}_2\text{CN}_2 \xrightarrow{\Delta} \text{PhCN} = \text{O} \xrightarrow{\Theta} 2 \text{PhC} = \text{O} + \text{N}_2 \]
Use of aqueous media simplifies the product mixtures by decreasing formation of olefins and azines, and deoxygenation removes the likelihood of benzophenone formation, leaving benzhydrols as the major products. Thus, first-order rate coefficients for decomposition of 1-Z could be extracted using Eq. 7. Examination of the kinetic results in Table 14 reveals the equivalence of $k_{obs}$ and $k_1$ for diphenyldiazomethane (1) under the conditions studied.

Substituted diphenyldiazomethanes also demonstrate first-order decomposition behavior at 75.0 °C at the concentrations employed. The unimolecular rate constants are listed in Table 15. Values of $k_1$ are (once again) found to be identical to those of $k_{obs}$ for the substituted diphenyldiazomethanes.

As expected, the major products of decomposition of 1-Z in aqueous glyme are the corresponding benzhydrols. From diphenyldiazomethanes 1-Z containing resonance electron-donating substituents ($Z = Cl, CH_3, OCH_3$), minor amounts of benzophenone azines 2-Z and traces of benzophenones 5-Z are obtained. The minor products resulting from decomposition of electron-deficient diphenyldiazomethanes (1-Z, $Z = CF_3, SO_2CH_3, CN, NO_2$) are dramatically different in that azines are not formed. Traces of ketones 5-Z are formed, however, from the latter diazo compounds. Thus, for electron-deficient diphenyldiazomethanes, $k_2$ is essentially zero and $k_{obs} = k_1$.

Regardless of the product compositions, it is immediately obvious (Table 15) that all substituents accelerate unimolecular decay relative to the parent diphenyldiazomethane 1. The correlation of the rate coefficients with resonance-enhanced Hammett substituent
constants in Table 5 is paraboloid (Fig. 2). Similar deviations in free-energy relationships have been noted in systems in which there is a change in mechanism, or a change in the rate-determining step of the same mechanism, with a concomitant change in substituent. Clearly, neither of these situations applies for thermal decompositions of diphenyldiazomethanes.

Correlations of the rate constants for the diphenyldiazomethanes with ground state substituent effects, as revealed by the $^{13}$C-NMR shieldings of the carbon in the diazo groups (Fig. 3), gives a parabolic correlation strongly resembling the previous Hammett free-energy relation (Fig. 2). The conclusion has thus been made that substituent effects in the transition states for decompositions of diphenyldiazomethanes are primarily responsible for the observed kinetic behavior.

Quantitative interpretation of the kinetic results is accomplished by dividing the substituents into two subgroups based upon electronic character, retaining the parent diphenyldiazomethane in both groups. As demonstrated in Fig. 1, correlations with $\sigma^+$ and $\sigma^-$, respectively, are somewhat curved, indicating deviation in the transition states for decomposition of 1-Z as compared to those for hydrolysis of cumyl halides\textsuperscript{46}, or phenol acidity\textsuperscript{47}, for which the basis sets were originally established.

Yukawa and Tsuno\textsuperscript{48} have derived an equation which adds a second reaction constant to the Hammett correlation (Eq. 9 and 10) in which $r$ is a measure of direct conjugative interactions and $\rho$ is the reaction constant expected for meta-substituent effects.
Table 14

Kinetic Parameters for Decomposition of Diphenyl-diazomethane in 2.18 M H₂O/1,2-Dimethoxyethane at 75 °C

<table>
<thead>
<tr>
<th>[1] (M)</th>
<th>10³k_{obs} (min⁻¹)</th>
<th>10³k_1 (min⁻¹)</th>
<th>k_2/k_3</th>
<th>10⁴[2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.65</td>
<td>1.59</td>
<td>1.59</td>
<td>6.05</td>
<td>3.54</td>
</tr>
<tr>
<td>1.65</td>
<td>1.60</td>
<td>1.60</td>
<td>6.05</td>
<td>3.59</td>
</tr>
<tr>
<td>1.57</td>
<td>1.54</td>
<td>1.52</td>
<td>4.05</td>
<td>2.14</td>
</tr>
<tr>
<td>1.57</td>
<td>1.60</td>
<td>1.51</td>
<td>4.05</td>
<td>2.10</td>
</tr>
<tr>
<td>1.57</td>
<td>1.56</td>
<td>1.58</td>
<td>4.05</td>
<td>2.38</td>
</tr>
</tbody>
</table>

a Calculated employing Eq. 7

Table 15

Unimolecular Rate Coefficients and Hammett Substituent Constants for Thermolyses of Substituted Diphenyldiazomethanes in 2.18 M H₂O/1,2-Dimethoxyethane at 75 °C

<table>
<thead>
<tr>
<th>Z</th>
<th>10³k_1 (min⁻¹)</th>
<th>Hammett Substituent Constants^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.55 ± 0.06^b</td>
<td>0.00 0.00 0.00</td>
</tr>
<tr>
<td>4-Cl</td>
<td>2.15 ± 0.07</td>
<td>0.27 0.11</td>
</tr>
<tr>
<td>4-CH₃</td>
<td>2.56 ± 0.16</td>
<td>-0.12 -0.31</td>
</tr>
<tr>
<td>4-OCH₃</td>
<td>8.14 ± 0.23</td>
<td>-0.16 -0.78</td>
</tr>
<tr>
<td>4-CF₃</td>
<td>2.68 ± 0.10</td>
<td>0.53 0.65</td>
</tr>
<tr>
<td>4-SO₂CH₃</td>
<td>3.58 ± 0.08</td>
<td>0.69 0.98</td>
</tr>
<tr>
<td>4-CN</td>
<td>3.90 ± 0.12</td>
<td>0.69 0.99^c</td>
</tr>
<tr>
<td>4-NO₂</td>
<td>6.68 ± 0.28</td>
<td>0.78 1.24</td>
</tr>
<tr>
<td>4-CH₃/4'-NO₂</td>
<td>11.10 ± 0.33</td>
<td>--- 1.07^d</td>
</tr>
</tbody>
</table>


^b Standard deviation


^d Calculated assuming direct additivity, i.e. \( \sigma^-_{NO₂} + \sigma^+_{CH₃} \)
Figure 2: Correlation of the rate coefficients for unimolecular thermal decomposition of diphenyldiazomethanes with Hammett resonance-enhanced constants.

Figure 3: Comparison of kinetic and ground state substituent effects in diphenyldiazomethanes.
\begin{align*}
\log k &= \rho (\sigma + r(\sigma^+ - \sigma)) + \log k_0 \\
\log k &= \rho (\sigma + r(\sigma^- - \sigma)) + \log k_0
\end{align*}

Both equations are improved by substitution of \(\sigma^0\) for \(\sigma\) (based upon hydrolysis of esters of substituted phenylacetic acids) since \((\sigma^+ - \sigma^0)\) measure better the conjugative ability of a substituent. Application of Yukawa-Tsuno theory to the decompositions of diphenyldiazomethanes gives Equations 11 and 12, indicating large resonance contributions of the substituent effects, thus extensive bond breakage in the transition states.

\begin{align*}
\log k &= -0.12 (\sigma^0 + 9.5 (\sigma^+ - \sigma^0)) - 2.816 \\
\log k &= +0.11 (\sigma^0 + 10.0 (\sigma^+ - \sigma^0)) - 2.805
\end{align*}

Any mechanistic theory for decomposition has to explain not only the rate-enhancing effect of all substituents, but the large acceleration in decomposition of 4-methyl-4'-nitrodiphenyldiazomethane resulting from addition of a 4'-methyl substituent to (4-nitrophenyl)-phenyldiazomethane (Table 5). Subtle control of the electronic distribution in the developing carbene by the substituent (Eq. 13 and 14) can explain the behavior of the mono-substituted diphenyldiazomethanes.
Electron-donor substituents are seen to favor development of an empty $p$-orbital (Eq. 13) and electron-withdrawers can overlap favorably with an electron-rich $p$-orbital (Eq. 14). This explanation is inconsistent, however, with the results with 4-methyl-4'-nitrodiphenyldiazomethane.

Extensive bond-breakage in the transition state as demonstrated by the mathematical correlations implies two highly developed atomic orbitals on diazo carbon, a $p$-orbital and a $sp^2$ orbital. Twisting of the phenyl rings resulting in overlap with either of these orbitals allows for stabilization of the developing carbene by electron-withdrawing or electron-donating substituents, as well as by both phenyl rings. This interpretation requires the aromatic rings to be twisted out of coplanarity, as well as non-linear extrusion of nitrogen (Fig. 4), and rehybridization to two "$sp^3$-like" orbitals in the transition state.
The actual electronic structure of the singlet carbene formed, while predicted energetically to be in the ground state with an empty p-orbital, is not clearly defined by this study. The nature of the intermediate is thus left open to question.
Chapter IV
RESULTS AND DISCUSSION

Thermolysis of substituted diphenyldiazomethanes\textsuperscript{44} has shown that any para-substituent (as compared to H-), regardless of its electronic character, enhances the rate of extrusion of nitrogen from the diazo compound to form diphenylmethylene. This observation has been explained to be the result of "orbital preference", whereby the electrical nature of the substituents dictates the alignment of each aromatic ring in the transition state for decomposition of a diphenyl-diazomethane (Fig. 5). A phenyl ring containing a para-electron withdrawer such as NO\textsubscript{2}, CN, or SO\textsubscript{2}CH\textsubscript{3}, is thus believed to overlap with the electron-rich orbital in the developing carbene, and similarly, an electron-donor such as OCH\textsubscript{3} or CH\textsubscript{3} donates into an electron-poor orbital, providing stabilization during formation of the intermediate.

These favorable interactions are presumed to be maximized when the phenyl rings are mutually perpendicular. Such a conformation may be readily obtained during loss of nitrogen from a diphenyldiazo-methane, in that rotation of its benzene rings should not be difficult. It thus became of interest to study substituent effects on the decompositions of diazo compounds in which such movement of the conjugating rings is restricted.
Figure 5: Orbital Preferences. Favored spatial alignment of aromatic rings in decomposition of diphenyldiazomethanes.

The basic thrust of the present work was to study thermolysis of a diazo compound similar in structure to diphenyldiazomethane, but in which little or no rotation of the phenyl rings is allowed. Ideally, the rings would be coplanar with the diazo group and rigidly held throughout decomposition. Para-substituent effects on the rates of thermolysis would be measured, and the differences and similarities between decomposition of the fixed-ring compound and of diphenyldiazomethane analyzed.

9-Diazofluorene (1) was the initial molecule chosen for study since it is expected to satisfy the requirement of maintaining the coplanarity of its aromatic rings during carbenic decomposition.

The benzenoid rings in 1 do not have rotational freedom and thus the π-systems in those rings can only overlap with the developing p-orbital in the singlet transition state leading to fluorenylidene carbene (1s). Precisely which intermediate forms depends upon the mode of nitrogen extrusion (Eq. 1). Non-linear extrusion of nitrogen leads to a rehybridization to two "sp³-like" orbitals which transform
to leave the lower energy $\sigma^2$ singlet. Linear decomposition provides the higher energy $p^2$ singlet.

\[
\begin{align*}
\text{non-linear} &
\begin{array}{c}
\text{linear}
\end{array}
\end{align*}
\]

Thus, if "orbital preference" is indeed mainly responsible for the observed thermal kinetic behavior of diphenyldiazomethanes, then substituents Z in 1 should primarily affect the p-orbital during loss of nitrogen, and electron-donating substituents should have the opposite effect from electron-withdrawers on the rates of decomposition, regardless of which transition state in Eq. 1 is involved. Electron-donors will thus lower the energy for generation of lower energy singlet $\sigma^2$ fluorenylidene (1s), while electron-withdrawers will slow the rate of formation of $\sigma^2$ 1s. The reverse will be true for formation of $p^2$ fluorenylidene. Thus, some kind of linear free-energy relationship might be found for decomposition of substituted
diazofluorenes, as opposed to the parabolic correlation observed for diphenyldiazomethanes.

It has been shown previously\textsuperscript{43} that hydroxylic solvents in decompositions of aryldiazo compounds greatly simplify product distributions by decreasing the amounts of azines formed (Eq. 2). This is important in study of first-order decompositions of diazo compounds, as the amounts of competing second-order processes are minimized in these media.

\[
\begin{align*}
\text{Ar}_2\text{C} = \text{N}_2 & \xrightarrow{k_1} \text{Ar}_2\text{C} = \text{N} = \text{N} = \text{C} \text{Ar}_2 \\
\text{Ar}_2\text{CN}_2 & \xrightarrow{k_2} \text{Ar}_2\text{C} = \text{N} = \text{C} \text{Ar}_2 \\
\text{Ar}_2\text{CSH} & \xrightarrow{k_3} \text{Ar}_2\text{CHSH}
\end{align*}
\]

\textbf{4.1 DERIVATION OF KINETIC METHOD}

Decomposition of 1 was first investigated in 2.18 M water/glyme (1,2-dimethoxyethane). Thermolysis of 1 was followed by visible spectroscopy since the C=N\textsubscript{2} band is very separate and distinct, allowing for accurate determinations of concentrations. The diazo band in 1 absorbs at 460 nm with an extinction coefficient of 29.1. Reliable measurements of diazo absorption in 1 can be carried out on concentrations of 10\textsuperscript{-2} M.
Reaction vessels were ground-glass stoppered quartz spectrophotometric cells, which were held in a Beckman DU spectrophotometer thermostatted at 75 °C. The initial thermal decompositions resulted in large increases in absorbances of the solutions, rather than the expected decreases. Clearly, some product of the reaction is absorbing strongly at the absorbance maximum of 9-diazofluorene (1).

Subsequent investigation revealed three important points: 1) 9-diazofluorene (1) has a long half-life, 19 h at 100 °C,\(^{49}\) 2) bifluorenylidene (2), a possible product of thermolysis of 1, has an intense \(\lambda_{\text{max}} \) (10^4) at 460 nm,\(^{50}\) and 3) 2 is reported to form from decomposition of 1 (Eq. 3) in up to 39% yield.\(^{51}\) Bifluorenylidene (2) is thus believed to result from reaction of fluorenylidene 1s with 1 with elimination of nitrogen. Under the above conditions, dimerization of 1s to 2 is highly improbable.

\[
\begin{align*}
\text{I} & \xrightarrow{\Delta} \text{I}s & \text{I}s & \xrightarrow{-N_2} \text{2} \\
\lambda_{\text{max}} &= 460 \text{ nm} \quad \varepsilon = 29.1 & \lambda_{\text{max}} &= 460 \text{ nm} \quad \varepsilon \sim 10^4
\end{align*}
\]

If disappearance of 1 by a second-order process is considerable, a reliable rate constant for first-order decomposition becomes impossible to obtain. It is necessary, then, to minimize, or better, to eradicate, any second-order contributions to the kinetic process. Because of the analytical method used, the great difference in the extinction coefficients of diazo compound 1 and product olefin 2
exaggerates the difficulties caused by second-order formation of 2. What might appear to be *kinetically* insignificant amounts of 2 (< 5%) formed result in sharp *increases* in visible absorbance, exceeding the absorbance limits of the Beckman spectrophotometer used for analysis. Hence, in the present system, formation of 2 must be completely suppressed.

To determine the extent to which 2 is formed, decomposition of 1 was effected at 75 °C in 2.18 M water/glyme on a larger scale, and the products separated by thin-layer chromatography. Isolation of bifluorenylidene (2) in greater than 5% yield indicated the severity of the problem. Bifluorenylidene (2) is a bright red crystalline solid which was characterized by comparison with an authentic sample from an independent synthesis. Facilitation of unimolecular thermal decomposition of a diazo compound is generally accomplished via two methods - a) increasing the rate of decomposition, and thereby decreasing the probability for collisions of remaining 1 and carbene 1s, by raising the reaction temperature and b) using more efficient agents for capture of 1s. It was hoped that these methods would eliminate formation of 2 and allow the reaction to be followed by visible spectroscopy.

Solvent systems studied initially were mixtures of alcohols and ethers. The alcohols were to function as nucleophiles for interception of 1s. The boiling point of a mixture had to be high enough to allow its use for practical decomposition of 1. Water in diglyme (bis-2-ethoxyethyl ether) at 95 °C was the initial solvent system
studied for decomposition of 1 at higher temperature. Reactions were
effected in the solvent mixture degassed by freeze-thaw techniques and
the products were analyzed by preparative thin-layer chromatography.
Attempts were made to follow the process kinetically by visible spec-
troscopy, quenching aliquots at 0 °C and determining their absorbances
at 460 nm. Formation of 5-10% of 2 at 95 °C indicated that the tem-
perature increase had not resulted in a significant decrease in olefin
formation, and the kinetic data were not useable (Eq. 4).

\[
\begin{align*}
\text{SH} &= \text{a) } 4.44 \text{ M H}_2\text{O/diglyme, 95 °C} \\
&= \text{b) } \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH, 135 °C} \\
&= \text{c) } \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH/diglyme, 150 °C} \\
&= \text{d) } (\text{C}_2\text{H}_5)_3\text{SiH, 107 °C} \\
&= \text{e) } (n-\text{C}_3\text{H}_7)_3\text{SiH, 173 °C}
\end{align*}
\]

Decomposition of 1 in degassed ethyl cellosolve (ethylene glycol
monoethyl ether) at 135 °C or in ethyl cellosolve in diglyme at 150 °C
gave substantial quantities of 2 and thus the systems could not be
used for determining the rate of decomposition of 1.

As it became clear that increasing the rate of decomposition of 1
in hydroxylic solvents would not suppress formation of 2, efforts were
made to increase the reactivity of the carbene capturing agent. Si-H
bonds are some of the best capturers of carbenes known. These bonds are some ten times more reactive than their hydroxylic counterparts. It was hoped that use of the tertiary silanes, triethylsilane and tri-n-propylsilane, would enhance the rates of interception of 1s and retard formation of 2.

Solubility of 1 in the pure silanes did not prove to be a problem. Decompositions of 1 in the silanes were conducted and analyzed as before. Upon refluxing 1 in degassed triethylsilane at 107 °C, red bifluorenylidene 2 was indicated by thin-layer chromatography and then by isolation in 5-10% yields. Once again, problems involving bimolecular coupling and determination of the concentrations of 1 during reaction were still present. Trials with tri-n-propylsilane at its reflux temperature of 173 °C similarly resulted in production of 2. After much experimentation and concern, it was decided that the kinetic stability of 1 and its propensity for forming 2 thermally in solution were impossible obstacles to overcome.

Study was then directed to determination of the kinetics of thermolysis of 10-diazoanthrone (3). 10-Diazoanthrone (3) was selected for investigation because a) coplanarity of its phenyl rings is maintained during decomposition, b) its carbonyl function is expected to destabilize 3 relative to 9-diazofluorene, and c) it posed less of a problem for analysis, since its extinction coefficient is much larger than that of 1, allowing use of more dilute solutions (10^{-4} M) and less interference of side products.
Exactly how the carbonyl group would affect formation of 10-anthronylidene 3a was unknown. Thermal decomposition is expected to generate the singlet carbene. Calculations for the $p^2$ singlet and the $\sigma^2$ singlet have shown that there is little energy difference between the carbenes (Fig. 6).\textsuperscript{55} A strong argument can be made for formation of $p^2$ 3a since the electrons can be delocalized on the carbonyl oxygen. In the cases of diphenyldiazomethane and 9-diazo-fluorene (1), there is no such stabilization for the $p^2$ carbene and thus the lower energy $\sigma^2$ carbene is expected to be produced.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.png}
\caption{Possible singlet carbenes generated from thermal decomposition of 3.}
\end{figure}

Regardless of which singlet state 10-anthronylidene is formed, any free-energy correlation of substituted 10-diazoanthrones is expected to be linear, as was expected for 9-diazofluorenes if orbital preference is primarily responsible for the behaviors of these types of molecules and if the mechanism for decomposition of 10-diazo-anthrone and diphenyldiazomethane are the same.
10-Diazoanthrone was synthesized (85%) from 9-anthrone (4) by treatment of 4 in the dark with \( \text{p-toluenesulfonyl azide} \) and sodium hydroxide in the presence of tetra-\( n \)-butylammonium bromide (Eq. 5).\(^{56} \) This synthetic method has previously been used to prepare 3 in the absence of a phase-transfer catalyst.\(^7 \) Addition of the catalyst results in increased yields under much milder and more dilute conditions than previously used and allows for a simpler and cleaner work-up. The structure of 3 was confirmed from its IR, NMR, and mass spectra.

\[
\text{O} \quad \text{TsN}_3 \text{OH} \quad \text{CH}_2 \text{Cl}_2, \text{RT} \quad \text{(n-Bu)}_4 \text{N}^+\text{Br}^- \quad \text{O} \quad \text{N}_2 \text{O}
\]

Decomposition of 3 was effected in refluxing tri-\( n \)-propylsilane at 173 °C. The thermolysis was carried out precisely as previously described for 9-diazofluorene (1). The high temperature and efficient capturing agent were implemented to favor first-order decomposition as best possible. Unlike 1, decay of 3 occurred rapidly, spectroscopic evidence for its presence was virtually non-existent within 30 min, and the spectrophotometric methods available were useable for following the reaction.

Attention was then given to hydroxylic solvents and lower temperatures for decomposition of 3. Thermolysis of 3 in ethyl cellosolve at reflux (135 °C) was too rapid to be followed accurately by the present kinetic method. Carbene generation at 100 °C which could be
monitored spectroscopically was observed, however, when decomposition was carried out in 4.44 M water/diglyme, the same water/diglyme composition used for thermolysis of 1.

The products of decomposition of 3 in the various capturing media were then determined. In all experiments, anthraquinone (5) is the major product. 10-Substituted anthrones, expected insertion products, are not isolated from any experiment, and appear to be transformed into 5 during chromatography. A minor product (< 5%) of the thermolysis is anthraquinone azine (6, Eq. 6). Azine 6 presumably results from capture of 10-anthronylidene by 3. The structures of quinone 5 and azine 6 were confirmed by comparison with authentic samples.7

\[\text{3} \xrightarrow{\Delta \text{SH}} \text{5} \]

\[\text{6}\]

\[\text{SH} = \begin{array}{l}
a) (n-C_3H_7)_3SiH, 173 ^\circ C \\
b) C_2H_5OCH_2CH_2OH, 135 ^\circ C \\
c) 4.44 \text{ M } H_2O/diglyme, 100 ^\circ C \\
\end{array} \]

Ketones from decompositions of diazo compounds are thought to arise via a second-order reaction with oxygen (Scheme I)45, just as azines and olefins such as bifluorenylidene (2) result from second-order processes. Formation of ketones thus also must be suppressed in
order to determine accurately the rates of first-order loss of nitrogen from diazo compounds.

As has been described previously, difficulties with oxygen contamination have been encountered (and overcome) in thermal decompositions of substituted diphenyldiazomethanes. Freeze-thaw techniques for solvent degassing were thus employed in the present work. These procedures involve handling large volumes of solvent (100 ml-250 ml) by syringe for the dilute solutions (10^{-4} M) necessary for accurate kinetic determinations. Such transfers may have allowed the trace oxygen contamination for which 10-diazoanthrone (3) is extremely susceptible.

Attempts to simplify the purification procedure led to the use of a single pure solvent for capture of carbene 3a. Since 3 is not soluble in water, the decompositions were effected in alcohols. 1-Propanol was selected for its boiling point (97 °C), availability, and ease of purification. Thermolyses of 3 in 1-propanol were run at reflux at 10^{-4} M concentrations using the methods outlined previously for 1. The 1-propanol was degassed using freeze-thaw techniques at
vacuum pressures below 10 microns in order to eliminate oxygen thoroughly from the system.

Linear first-order plots were indeed obtained for thermolyses of 3 in 1-propanol at 97 °C. The rate constants for decomposition, however, were not reproducible (Table 16).

Table 16

<table>
<thead>
<tr>
<th>$10^3 k$ (min$^{-1}$)</th>
<th>$r^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.83</td>
<td>-0.997</td>
</tr>
<tr>
<td>1.31</td>
<td>-0.996</td>
</tr>
<tr>
<td>1.43</td>
<td>-0.998</td>
</tr>
</tbody>
</table>

$a$ Correlation coefficient for line

A concern then became, since a pure alcohol had been used neat and thus the capturing agent was in large excess, that a pseudo first-order process was occurring as illustrated in Scheme II, involving direct reaction of diazo compound 3 with solvent. It is possible that ylid 7 is thus formed and then rearranges to 10-alkoxyanthrone 8.

Control experiments were then conducted with 1-butanol as solvent at 117 °C to distinguish between the two modes of reaction. Experiments were conducted in neat 1-butanol and with 1-butanol in much lower concentration in diglyme. The difference in the rate constants observed is less than 10% (Table 17), and is deemed insignificant since a 3000-fold rate increase is expected if a second-order reaction with the solvent were occurring.
Table 17
Rates of Decomposition of $9 \times 10^{-5}$ M 10-Diazoanthrone (3) in Media of Different Compositions at 117 °C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$10^3 k_{obs}$ (min$^{-1}$)</th>
<th>$r^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-BuOH</td>
<td>7.92</td>
<td>-0.985</td>
</tr>
<tr>
<td>$3.63 \times 10^{-4}$</td>
<td>8.41</td>
<td>-0.978</td>
</tr>
<tr>
<td>1-BuOH/diglyme</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Correlation coefficient for line.

These results agree with previous decompositions of diphenyldiazo­methane$^{43}$ and 2,6-di-t-butyl-1,4-benzoquinonediazide$^{57}$ in that only slight rate enhancements occur upon increasing greatly the concentration of capturing agents.
Having demonstrated that the observed straight-line plots of \( \ln A \) vs. time come from first-order decomposition processes, the problem of irreproducible rate constants remained. When \( \ln A \) vs. time is plotted for runs in 1-propanol, 1-butanol, and various solvent mixtures, the lines exhibit some curvature (Fig. 7). The extent and degree of curvature, as well as the positions of initial deviation from linearity, vary randomly.

![Graph](image)

**Figure 7:** Depiction of graphical analysis of decompositions of \( \cdot 10 \)-diazoanthrone in varied solution compositions.

This curvature was believed to be caused by a buildup of products, including the azine 6, which has significant visible absorption at 405 nm, the maximum absorption wavelength for the diazo band in 3. It was presumed that oxygen is involved in these processes, possibly causing radical and oxidation reactions, and efforts were intensified to improve the deoxygenation method.

After many attempts at changing the amount of solvent, the reaction vessel, and the vacuum pressures, including the use of vacuum
line techniques (< 5 microns), rate constants were still not reproducible. In all of these experiments, a transfer operation under an inert atmosphere was required somewhere in the procedure. It was concluded that the above transfers could not be carried out sufficiently oxygen-free for these decompositions. The reaction mixtures (solutions of 3 in freshly distilled 1-butanol) would have to be deoxygenated and the decompositions would have to be run in the same vessel. Further, 1-butanol being used in large amounts would have to be more efficiently degassed. Hence, visible cells were designed which were equipped with high-vacuum valves (Fig. 8), and the reaction mixtures were degassed by extensive freeze-thaw processes in darkness as described in detail in the experimental section.

Figure 8: Diagram of reaction cell used for decompositions of 3.
After degassing its contents, the reaction cell was warmed to room temperature and then placed in a constant temperature oil bath. Concentrations at appropriate time intervals were measured by reading visible absorbances of the solutions during reaction. The rigorous experimental methods described resulted in reproducible rate constants (Table 18). There were none of the deviations from linear plots as had been previously observed. Moreover, use of quartz cells gave data improved from that of Pyrex cells.43

| Decompositions of Scrupulously Degassed Solutions of 3 in 1-Butanol at 110 °C |
|---------------------------------|---------------------------------|
| $10^4[3]$ (M) | $10^3k_{obs}$ (min⁻¹) |
| 1.18 | 6.22 ± 0.05a |
| 1.24 | 6.13 ± 0.06 |
| 1.36 | 5.87 ± 0.05 |
| 1.44 | 5.72 ± 0.05 |
| 0.745 | 6.31 ± 0.02 |
| 0.865 | 6.43 ± 0.01 |

a Standard deviation for the line

Subsequent experiments were conducted in quartz, and the data obtained were satisfactorily consistent. A viable kinetic method for accurate determination of first-order rate constants for decomposition of 3, a highly oxygen-sensitive diazo compound, had thus been established.

4.2 SYNTHETIC METHODS

Having demonstrated the reliability of the kinetic method for 10-diazoanthrone (3), study was extended to synthesis of
2-substituted-10-diazoanthrones (3-Z). Where in 3-Z the substituent is a resonance electron-donor (Z = OCH\(_3\), CH\(_3\), or Cl), synthesis of diazoanthrones was accomplished via Scheme III. The precursor 2-substituted-9-anthrones (4-Z) were prepared by adaptation of literature procedures.\(^5\)

Thus, Friedel-Crafts acylation of the appropriately substituted benzenes (Z-Ø) by phthalic anhydride with aluminum chloride (> 2 equiv) at 90-100 °C forms exclusively the 4'-substituted-2-benzoylbenzoic acids (9-Z) in good yields (81-87%). The structures of the acids 9-Z were assigned from their melting points and IR and NMR spectra. Reductions of the 4'-substituted-2-benzoylbenzoic acids (9-Z) with zinc/copper in refluxing aqueous ammonia afford the corresponding 4'-substituted-2-benzylbenzoic acids (10-Z) in 80-90% yields. Spectral methods (IR and NMR) were used for identification. Anthrones 4-Z result from treatment of acids 10-Z with concentrated
sulfuric acid at 0 °C. The structures of the 2-substituted-9-anthrones were confirmed by spectral evidence (IR and NMR) and by their melting points.

2-Substituted-10-diazo-9-anthrones 3-Z were then prepared from precursor 2-substituted-9-anthrones 4-Z by base-catalyzed reactions with p-toluenesulfonyl azide. As found in synthesis of 3, reactions of 4-Z with p-toluenesulfonyl azide (1 equiv) and sodium hydroxide (10 equiv) in methylene chloride are much more effective in the presence of tetra-n-butylammonium bromide. The phase-transfer catalyst allows reaction to be carried out at room temperature (5 h) in very dilute solution. The diazo transfer processes proceed best in the absence of light. These conditions minimize the formation of 2,2'-disubstituted anthraquinone azines 6-Z.

Purification of the 2-substituted-10-diazoanthrones to kinetic standards was accomplished by preparative thin-layer chromatography on silica gel and crystallization from chloroform/hexane. The purities were confirmed by quantitative elemental analysis. The structures of 3-Z were established by IR, NMR, UV-visible, and mass spectral methods. The IR spectra have their strongest bands at 2060-2080 cm\(^{-1}\) (C=N=N stretches) and 1630-1650 cm\(^{-1}\) (C=O stretches). The NMR spectra
are distinguished by the downfield separation (δ 0.5-1.0 ppm) of aromatic hydrogens peri- to the diazo moiety and by the absence of methylene absorptions (CH₂) from precursor anthrones 4-Z.

The diazo groups in 3-Z absorb in the visible at 400-430 nm with extinction coefficients of 10⁴. The mass spectra for 4-Z are characterized by their M⁺, M - 28 (loss of N₂), and M - 56 (loss of N₂ and CO) peaks. When Z is resonance electron-withdrawing, such as for Z = NO₂, CN, SO₂CH₃, or CF₃, electrophilic processes such as Friedel-Crafts acylation on Z-0, or ring-closure (as in Scheme III) to give 4-Z are not effective. In the present research, it was desirable to synthesize 2-nitro-, 2-cyano, and 2-carbomethoxy-10-diazo-9-anthrones in order to study the effects of electron-withdrawal on the rate of decomposition of 3. None of the precursor anthrones 4-Z, 2-nitroanthrone, 2-anthronecarbonitrile, or methyl 2-anthronecarboxylate, is known.

Attempts were first made to prepare 4-NO₂. As illustrated in Scheme IV, 2-bromo-4-nitrotoluene (11) reacts with cuprous cyanide in dimethylformamide to yield 2-methyl-5-nitrobenzonitrile (12, 71%) conveniently. 59

Hydrolysis of 12 in aqueous sulfuric acid at 180 °C gives 2-methyl-5-nitrobenzoic acid (13, 55%) 60 which is converted to
2-methyl-5-nitrobenzophenone (14, 77%)\textsuperscript{61} by treatment with thionyl chloride and then benzene and aluminum chloride at 35 °C.

Scheme IV

\[
\begin{align*}
\text{CH}_3 \\
\text{Br} & \quad \text{CuCN} & \quad \text{DMF} & \quad \text{CH}_3 \\
\text{NO}_2 & \quad \text{CN} & \quad 70\% \text{H}_2\text{SO}_4 & \quad \text{CO}_2\text{H} \\
\text{11} & \quad \text{12} & \quad \text{13} \\
\end{align*}
\]

Bromination of 2-methyl-5-nitrobenzophenone (14) to 2-bromo-methyl-5-nitrobenzophenone (15) for closure to 2-nitro-9-anthrone was then planned (Eq. 7). Photolytic bromination of 14 with N-bromo-succinimide in refluxing carbon tetrachloride yielded a mixture of benzyl bromide 15 (~70%, δ 4.65, -CH\textsubscript{2}Br) and 2,2-dibromomethyl-5-nitrobenzophenone (~20%, δ 7.03, -CHBr\textsubscript{2}). Attempts to separate and purify 15 by chromatography on silica gel and recrystallization from hexane result in its alteration to a product having no bromine and no resonance signal for a methylene group, either for benzyl halide 15 or anthrone 4-NO\textsubscript{2}.

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{NBS} & \quad \text{CCl}_4 & \quad \text{O}_2\text{N} & \quad \text{AlCl}_3 \\
\text{CH}_3 & \quad \text{O}_2\text{N} & \quad \text{CH}_2\text{Br} & \quad & \quad \text{O}_2\text{N} \\
\text{14} & \quad \text{15} & \quad & & \quad \text{4-NO}_2 \\
\end{align*}
\]

(7)
It is likely that during chromatography, 15 undergoes ring-closure and loss of hydrogen bromide as in Eq. 8 to give 3-nitro-1-phenylisobenzofuran (16). Indeed, 2-bromomethylbenzophenone is thermally instable and converts readily to 1-phenylisobenzofuran. Ring closure of 15 to 4-NO₂ could not be accomplished.

Additional possible approaches to synthesis of 4-NO₂ are illustrated in Eq. 9. It was hoped that 2-methyl-5-nitrobenzoic acid (13) could be brominated to 17, which would react with benzene and aluminum chloride to give 5-nitro-2-phenylmethylbenzoic acid (18), 2-bromomethyl-5-nitrobenzophenone (15), and/or 2-nitro-9-anthrone (4-NO₂). Either 18 or 15 could possibly be closed to 4-NO₂ as well.
Bromination of 13 was conducted with bromine in refluxing bromo-
form.\textsuperscript{63} NMR analysis of the product revealed two singlets, one for 13
(δ 2.72, 58%) and one at δ 5.48 (42%) corresponding exactly to the
methylene singlet of an authentic sample of 6-nitrophthalide (20).\textsuperscript{64}
Thus bromination does occur, only to be succeeded immediately by
lactonization of 17 to 20 (Eq. 10). 2-Bromomethyl-5-nitrobenzoic acid
was deemed to be an unsatisfactory precursor to 4-NO\textsubscript{2} since lactoniza-
tion is expected to take place at the temperatures required for
Friedel-Crafts reactions. Synthesis of 4-NO\textsubscript{2} was dropped.

\[
\begin{align*}
\text{CH}_3 & \text{CO}_2\text{H} \quad \rightarrow \quad \text{CH}_2\text{Br} \quad \rightarrow \quad \text{O}_2\text{N} \quad \text{O} \\
\text{Br}_2 & \quad \text{CHBr}_3 & \quad \text{CO}_2\text{H} & \quad \text{NO}_2 & \quad \text{20} \\
\text{13} & & \text{17} & & \text{20}
\end{align*}
\]  

(Eq. 10)

Study was then directed to synthesis of 2-anthronecarbonitrile
(4-CN). Cuprous cyanide displacements on chloronaphthalenes to give
nitriles are known.\textsuperscript{59} Thus, 2-chloroanthrone (4-Cl) was reacted with
cuprous cyanide in N,N-dimethylformamide, pyridine and N-methylpyrro-
lidone at 230-250 °C in attempts to prepare 4-CN (Eq. 11).

\[
\begin{align*}
\text{CuCN} & \quad \text{DMF} & \quad \text{N-Me pyrrolidone} & \quad \text{pyridine} \\
\text{4-Cl} & & & \quad \text{4-CN} \\
\end{align*}
\]  

(Eq. 11)

These reactions result in formation of intractables, and 2-chloro-
anthrone was deemed inadequate for cyanide displacement.
Since chlorides are more difficult to displace than bromides, 2-bromoanthrone (4-Br) was prepared and its possible conversion to 4-CN was investigated as outlined in Scheme V.

**Scheme V**

Friedel-Crafts acylation of bromobenzene by phthalic anhydride with aluminum chloride yields 2-(4'-bromobenzoyl)benzoic acid (9-Br, 86%). Modified Clemmensen reduction of 9-Br utilizing zinc/copper as for 9-Cl, 9-OCH$_3$, and 9-CH$_3$ did not give 10-Br cleanly. Considerable loss of bromine occurred in the reduction. A two-step reduction sequence involving triethylsilane$^{65}$ and then phosphorous and iodine was then found to afford 10-Br cleanly. Triethylsilane and 9-Br in trifluoroacetic acid at 25-30 °C yields 3-(4-bromophenyl)phthalide (21, 74%), a neutral compound identified by its melting point and IR (C=O at 1770 cm$^{-1}$) and NMR (singlet at $\delta$ 6.30) spectra. Phthalide 21 is then converted by phosphorous and iodine in refluxing glacial
acetic acid to desired acid 10-Br. 2-Bromo-9-anthrone (4-Br) was
generated (96%) from 10-Br by ring closure with concentrated sulfuric
acid at 0 °C. Air at room temperature was found to oxidize 4-Br to
2-bromoanthraquinone (5-Br) rapidly.

Reactions of cuprous cyanide with 4-Br in N,N-dimethylformamide,
N-methylpyrrolidone, or pyridine in pyrex bombs give complex mixtures.
2-Anthraquinonecarbonitrile (5-CN), the only isolable product from the
reactions, was identified by its mass spectrum (M+ = 233) and by the
absence of a methylene singlet in its NMR spectrum.

In displacements of aryl halides with cuprous cyanide, the
nitrile-cuprous cyanide complex must be destroyed in work-up by
heating to 60 °C with ferric chloride, ethylenediamine, or aqueous
sodium cyanide. It is presumed that 4-CN oxidizes in the air to 5-CN
during these procedures (Eq. 12). Thus, the present method was deemed
unsuitable for synthesis of 4-CN and no further efforts were made to
prepare the nitrile.

Interest then centered on synthesis of methyl 10-diazo-9-
anthrone-2-carboxylate (3-CO₂Me). Methyl 9-anthrone-2-carboxylate
(4-CO₂Me) and 3-CO₂Me were successfully prepared by the methods of
Scheme VI.
Scheme VI

4-Benzoyl-1,3-benzenedicarboxylic acid (22)\textsuperscript{66}, as prepared (84%) by oxidation of 2,4-dimethylbenzophenone with potassium permanganate in refluxing aqueous tert-butyl alcohol, was reduced by zinc/copper in ammonium hydroxide to white crystalline 4-phenylmethyl-1,3-benzenedicarboxylic acid (23, 77%) characterized spectrally and by its neutralization equivalent and melting point.\textsuperscript{66}

Ring closure of 23 by sulfuric acid occurs readily to yield 9-anthrene-2-carboxylic acid (4-CO$_2$H, 97%), a high-melting, difficultly soluble product assigned spectrally (IR and MS). Crude 4-CO$_2$H was converted efficiently by refluxing methanol containing concentrated sulfuric acid to methyl 9-anthrene-2-carboxylate (4-CO$_2$Me).\textsuperscript{67}
Ester \(4-CO_2Me\) is obtained (43%) pure by chromatography on silica gel. NMR singlets at \(\delta 3.93\) and \(\delta 4.28\) showed the presence of carbomethoxy and methylene groups, respectively, in \(4-CO_2Me\). Infrared absorption at 1720 cm\(^{-1}\) for ester carbonyl and 1660 cm\(^{-1}\) for ketone carbonyl and a molecular ion of 252.0799 mass units confirmed the structure of \(4-CO_2Me\).

Methyl 10-diazo-9-anthrone-2-carboxylate (\(3-CO_2Me\)) was then synthesized (83%) by diazo-transfer to \(4-CO_2Me\) in dichloromethane with \(para\)-toluenesulfonyl azide and sodium carbonate in the presence of \(tetra-n\)-butylammonium bromide. For preparation of \(3-CO_2Me\), sodium carbonate was used instead of sodium hydroxide in order to generate the anthronyl anion of \(4-CO_2Me\) without saponification of the ester moiety. Diazo ester \(3-CO_2Me\) is yellow-brown, shows proper elemental analysis, exhibits IR absorptions at 2075 (C=\(N_2\)), 1720 (CO\(_2\)Me), and 1640 (C=O) cm\(^{-1}\), has strong visible absorption at 406 nm (C=\(N_2\)) and shows NMR peaks at \(\delta 3.95\) (CO\(_2\)CH\(_3\)) and at \(\delta 9.12\) and \(\delta 8.50\) (downfield shifts for its aromatic protons). Identification of \(3-CO_2Me\) is further confirmed mass spectrally by its molecular ion (278.0162) and masses corresponding to loss of nitrogen (250.0589) and of nitrogen and carbon dioxide (222.0576).

All of the diazo compounds \(3-Z\) synthesized were purified to kinetic standards by preparative thin-layer chromatography and recrystallized from chloroform/hexane. 2-Substituted-10-diazo-anthrones are stable for long periods when stored under vacuum and in darkness.
4.3 KINETIC STUDIES

Solutions of 3-Z of known concentrations in 1-butanol were prepared for kinetic study and degassed by the scrupulous freeze-thaw methods described in the experimental section. Kinetic data were obtained by following the change in absorbance of each solution at the wavelength of maximum absorption in the visible spectrum. Runs consisted of three solutions each, and at least three experiments were conducted for each compound.

All reactions of 3-Z in 1-butanol at 100 °C are strictly first-order through two half-lives over the range of concentrations employed (5.0 \times 10^{-5} \text{ to } 1.2 \times 10^{-4} \text{ M}).

Observed rate coefficients, $k_{\text{obs}}$, are calculated by computerized least-squares fit of the data to an integrated form of the first-order rate expression:

$$A_t = A_0 \exp(-k_{\text{obs}}t) + A_\infty$$

and standard deviations for each plot determined by standard methodology. For all of the diazo compounds 3-Z, the kinetic data are highly reproducible within experimental error. Examples of these data are summarized in Table 19.

Examination of the kinetic parameters in Table 19 leads to the conclusion that resonance electron-donating substituents facilitate first-order loss of nitrogen from 3-Z at 100 °C, while electron-withdrawers retard the rate of decomposition. Half-lives for the thermolyses at 100 °C range from 2 hours for 3-CH$_3$ to 17 hours for 3-CO$_2$Me.
Table 19

Decomposition of Substituted 10-Diazoanthrones (3-Z) in 1-Butanol at 100 °C: Observed Rate Coefficients

<table>
<thead>
<tr>
<th>Z</th>
<th>$10^4 <a href="M">3-Z</a>$</th>
<th>$10^3 k_{obs}$ (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>8.18</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>10.9</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>6.36</td>
<td>1.39</td>
</tr>
<tr>
<td>Cl</td>
<td>5.72</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td>4.18</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>7.24</td>
<td>1.83</td>
</tr>
<tr>
<td>CH₃</td>
<td>9.40</td>
<td>2.44</td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>13.7</td>
<td>2.25</td>
</tr>
<tr>
<td>OCH₃</td>
<td>6.17</td>
<td>5.42</td>
</tr>
<tr>
<td></td>
<td>11.2</td>
<td>5.16</td>
</tr>
<tr>
<td></td>
<td>13.2</td>
<td>5.09</td>
</tr>
<tr>
<td>CO₂CH₃</td>
<td>7.19</td>
<td>0.668</td>
</tr>
<tr>
<td></td>
<td>8.72</td>
<td>0.685</td>
</tr>
</tbody>
</table>

Product analysis on a kinetic scale was attempted. Thin-layer chromatography showed two major products, neither being azines 6-Z. Identification of the products on a kinetic scale ($10^{-4}$ M, < 0.2 mg) was difficult, and thus macroscopic decompositions of 10-diazoanthrone 3 in 1-butanol ($10^{-2}$ M) were conducted under purified argon to determine the product composition. In all instances, anthraquinone (5) was formed in substantial yields, as identified by spectral methods. No 10-butoxyanthrone (24) was found. Thus, efforts were directed toward an independent synthesis of 10-butoxyanthrone, which is not known. Early work describes preparation of 10-methoxyanthrone (25) from
10-bromoanthrone (26) and methanol, and a similar approach was taken to 24 (Eq. 13).

\[
\begin{align*}
\text{H} & \text{Br} \\
\text{O} & \text{O} \\
\text{26} & \text{ROH} \\
\text{O} & \text{OR} \\
\text{24} & R = n-\text{Bu} \\
\text{25} & R = \text{CH}_3
\end{align*}
\]

(13)

10-Bromoanthrone\(^\text{69}\) was prepared from anthrone and bromine in carbon tetrachloride, and identified by its melting point and NMR spectra. Reactions of 26 with 1-butanol were carried out under acidic, basic, and neutral conditions under inert atmospheres. In all trials, anthraquinone was the isolable product.

Anthraquinone (5) may form from the hydroperoxide 27 which results from rapid reaction of alkoxyanthrone 24 (or its tautomeric anthranol) with air during work-up\(^\text{40}\) followed by decomposition of 27 to give alkoxy radical 28, which can strip hydrogen from the remaining 1-butanol, leaving butyraldehyde and a hemi-acetal 29 which hydrolyzes to 5 (Scheme VII).
An alternate possibility is for alkoxy radical 28 to lose butoxy radical and form 5 (Eq. 14).

It is clear from the kinetic data, however, that anthraquinone is a product formed after capture of the solvent 1-butanol by 3 to form 24. Thus, there is no effect of the product distribution on the first-order kinetics.

Lack of azines in the product mixtures and the first-order behavior exhibited by the diazo compounds demonstrate that $k_{obs}$ for the process is a reasonable approximation for $k_1$, the unimolecular decomposition constants for the reactions (Eq. 15). Calculations in previous work with decompositions of substituted diphenyl diazomethanes have shown that even where small amounts of products
resulting from second-order processes are formed, $k_{\text{obs}}$ is virtually identical to $k_1$.

\[ \text{O} \quad \xrightarrow{k_1} \quad \text{O} \quad \xrightarrow{k_{\text{slow}}} \quad \text{O} \quad \xrightarrow{\text{OnBu}} \quad \text{O} \quad \xrightarrow{\text{H}} \] (15)

The average unimolecular rate coefficients for the decompositions of the 10-diazoanthrones investigated at 100 °C are compiled in Table 20. Electron-withdrawing substituents decrease the rates of decomposition of substituted diazoanthrones 3-Z, unlike the effect observed in thermolysis of substituted diphenyldiazomethanes.

Table 20

Average Unimolecular Rate Coefficients for the Decompositions of 2-Substituted-10-Diazoanthrones (3-Z) in 1-Butanol at 100 °C

<table>
<thead>
<tr>
<th>Z</th>
<th>$k_{\text{obs}}$ (min$^{-1}$)</th>
<th>Hammett Substituent Constants$^a$</th>
<th>$\sigma^+$</th>
<th>$\sigma^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-OCH$_3$</td>
<td>5.23 ± 0.26$^b$</td>
<td>-0.79</td>
<td>-0.13</td>
<td></td>
</tr>
<tr>
<td>2-CH$_3$</td>
<td>2.35 ± 0.11</td>
<td>-0.31</td>
<td>-0.12</td>
<td></td>
</tr>
<tr>
<td>2-Cl</td>
<td>1.82 ± 0.11</td>
<td>0.11</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>2-H</td>
<td>1.40 ± 0.07</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>2-CO$_2$CH$_3$</td>
<td>0.677 ± 0.012</td>
<td>0.48</td>
<td>0.48</td>
<td></td>
</tr>
</tbody>
</table>


$^b$ Standard deviation
An excellent linear correlation of the rate constants for 3-OCH$_3$, 3-CH$_3$, 3-H, and 3-CO$_2$CH$_3$ with the corresponding Hammett resonance-enhanced substituent constants ($\sigma^+$) is illustrated in Fig. 9, and the relationship is quantitatively expressed in Eq. 16. The magnitude of the $\rho$ value (-1.62) indicates that there is a substantial substituent effect at the reaction center, and the negative sign of $\rho$ reveals that the transition state is electron-deficient.

$$\log k_{100^\circ C} = -1.62 \sigma^+ - 6.53 \quad s = 0.021 \quad (16)$$

2-Chloro-10-diazoanthrone (3-Cl) does not correlate with the resonance-enhanced substituent constants ($\sigma^+$). In correlations with $\sigma^+$, the Cl-substituent is expected to retard rates of formation of positive centers. 2-Chloro-10-diazoanthrone decomposes faster, however, than the parent 3-H.

The total electronic effect of a given substituent on a reaction center is a combination of its resonance and inductive influences. The degree to which each electrical component contributes to the overall result controls the final effect.

For most substituents (for a given position on a benzene ring), the two electronic component vectors combine for a larger effect than either alone (e.g. the $p$-NO$_2$ substituent removes electron density via both its resonance and field effects), or one vector overpowers the other (e.g. $p$-OCH$_3$ donates electron density via resonance to a much greater extent than the electronegative oxygen atom causes withdrawal), leaving a definitive combined effect. The effects in halogen
Figure 9: Hammett plot of rate constants vs. substituent effects for decomposition of 2-substituted-10-diazoanthrones in 1-butanol at 100 °C.
substituents, however, are less clear, and the relative magnitudes of the inverse mesomeric and inductive contributions dictate the overall electronic effect of a substituent.

Substituent effects resulting from multiple electronic contributions have frequently been quantitatively correlated by more refined methods. Addition of a second substituent and reaction constant to the Hammett equation results in Eq. 17.

$$
\log k = \rho (\sigma^0 + r(\sigma^+ - \sigma^0)) + \log k_0
$$

(17)

Here, in the Yukawa-Tsuno equation for electrophilic reactions, $r$ is a quantitative parameter reflecting the importance of direct conjugative interactions, and $\rho$ is the standard reaction constant expected for meta-substituents. The $\sigma^0$ substituent parameters are defined by the hydrolysis of esters of phenylacetic acids, where a methylene group intervenes, preventing resonance interaction between the substituent and the reaction center. Thus, $(\sigma^+ - \sigma^0)$ is a truer theoretical measure of conjugative interactions.

A correlation of the Yukawa-Tsuno type was made (Fig. 10) for thermolyses of the five substituted 10-diazoanthrones. As can be seen, the reaction rates of all substituted 3-Z are related by the linear free-energy methods resulting in Eq. 18. The results demonstrate marked resonance interaction of the substituent with the electron-deficient orbital developing at the reaction center in the transition state, as well as a smaller polar effect. Thus, the unusual behavior of the Cl-substituent for decomposition of 10-diazoanthrones is reasonably explained.
Figure 10: Yukawa-Tsuno plot of rate constants vs. separated substituent effects for the decomposition of 2-substituted-10-diazoanthrones in 1-butanol at 100 °C.
\[ \log k_{100^\circ C} = -0.570 \left( \sigma^0 + 3.26(\sigma^+ - \sigma^0) \right) - 6.51 \] (18)

The statistical calculations as presently summarized are regressions carried out on small data sets, and, as such, the absolute values of the rate coefficients might be questioned. It is emphasized, however, that the relative magnitudes of the results are what are important and lead to the conclusions drawn.

Decompositions were also conducted at 90 \(^\circ\)C and 106 \(^\circ\)C to study temperature effects on the processes and to determine thermodynamic parameters for the reactions. The temperature range was dictated largely by limitations of convenience in the analytical procedure. At least two trials of three cells each were run for all 3-\(Z\). The results of the experiments are compiled in Table 21. The rate constants at temperatures over 106 \(^\circ\)C for 3-\(OCH_3\) are unreliable, since the decompositions are too rapid to follow accurately.

The qualitative results at 90\(^\circ\)C and 106\(^\circ\)C duplicate those previously found (Table 22): electron-donation from 2-\(OCH_3\), 2-\(CH_3\), and 2-\(Cl\) substituents facilitate whereas electron withdrawal from the 2-\(CO_2CH_3\) substituent retards loss of nitrogen.

The four compounds 3-\(OCH_3\), 3-\(CH_3\), 3-\(H\), and 3-\(CO_2CH_3\) fit well on Hammett \(\sigma^+\) correlations at 90 \(^\circ\)C and 106 \(^\circ\)C. The reaction constant decreases from -1.77 to -1.59 (Eq. 19 and 20, Fig. 7), as the temperature is raised from 90 \(^\circ\)C to 106 \(^\circ\)C, as expected.
Table 21
Rate Constants for Decompositions of 2-Substituted-10-diazoanthrones 3-Z at 90 °C and 106 °C

<table>
<thead>
<tr>
<th>Z</th>
<th>10^3 k_{obs}</th>
<th>90 °C</th>
<th>106 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.599</td>
<td>3.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.608</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.597</td>
<td>3.05</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.754</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.670</td>
<td>3.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.738</td>
<td>3.48</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.07</td>
<td>5.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>4.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>4.74</td>
<td></td>
</tr>
<tr>
<td>OCH₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.53</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.44</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>CO₂CH₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.261</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.266</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.266</td>
<td>1.53</td>
<td></td>
</tr>
</tbody>
</table>

Table 22
Average Unimolecular Rate Constants for Decompositions of 2-Substituted-10-diazoanthrones in 1-Butanol at 90 °C and 106 °C

<table>
<thead>
<tr>
<th>Z</th>
<th>10^3 k_{obs} (min⁻¹)</th>
<th>90 °C</th>
<th>106 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.598 ± 0.029ᵃ</td>
<td>3.13</td>
<td>0.11</td>
</tr>
<tr>
<td>Cl</td>
<td>0.721 ± 0.036</td>
<td>3.45</td>
<td>0.11</td>
</tr>
<tr>
<td>CH₃</td>
<td>1.14 ± 0.05</td>
<td>4.80</td>
<td>0.15</td>
</tr>
<tr>
<td>OCH₃</td>
<td>2.46 ± 0.06</td>
<td>11.08</td>
<td>0.43</td>
</tr>
<tr>
<td>CO₂CH₃</td>
<td>0.266 ± 0.006</td>
<td>1.45</td>
<td>0.02</td>
</tr>
</tbody>
</table>

ᵃ Standard deviation
The increase in temperature lowers the free energy of activation when \( \Delta S \) is positive, causing earlier formation of a transition state whose less developed orbitals are less susceptible to substituent effects.

The Yukawa-Tsuno analyses (Eq. 21-22, Fig. 12 and 13) do not show any trend in the magnitudes of \( \rho \) and \( r \) with changes in temperature. At all temperatures studied, however, the resonance contributions of substituents to the transition states for decomposition of 2-substituted-10-diazoanthrones far outweigh their polar counterparts.

Thermodynamic parameters calculated for the decompositions are summarized in Table 23. These values result from regressions calculated from data sets of three points, and thus the statistical significance of the absolute values may be regarded with caution.

\[
\begin{align*}
\log k_{90^\circ C} &= -1.77 \sigma^\dagger - 7.39 \quad s = 0.046 \\
\log k_{106^\circ C} &= -1.59 \sigma^\dagger - 5.78 \quad s = 0.036
\end{align*}
\] (19) (20)

\[
\begin{align*}
\log k_{90^\circ C} &= -0.827 (\sigma^0 + 2.29(\sigma^\dagger - \sigma^0)) - 7.33 \\
\log k_{106^\circ C} &= -0.657 (\sigma^0 + 2.74(\sigma^\dagger - \sigma^0)) - 5.77
\end{align*}
\] (21) (22)
Figure 11: Hammett plots of rate constants vs $\sigma^+$ for decompositions of 2-substituted-10-diazoanthrones in 1-butanol at 90 °C and 106 °C.
Graphical analysis of ln k vs. 1/T gives a correlation coefficient of -0.988 or better for each compound (Fig. 14). The experimental error in determining the rate constant may be quite large for 2-methoxy-10-diazoanthrone because of its rapid decomposition and thus its activation parameters may be only approximate. All of the plots show some upward curvature, indicating a non-zero heat capacity for the transition states relative to the 10-diazoanthrones.

Values for the activation energies for the decompositions are, as expected, in inverse order to those for the rate constants. Electron donors lower the activation energy for loss of nitrogen, while electron-withdrawing substituents raise the activation energy by destabilizing formation of the transition state. The order of magnitude for $E_a$ of 25-29 kcal/mole is similar to that of diphenyl-diazomethane, which has an activation energy of about 27 kcal/mole. The entropies of activation (Table 23) show values near zero for all compounds studied, indicating little reorganization in the thermolysis transition states.

The results of the present research allow analysis of the mechanistic pathways for thermal decomposition of 10-diazoanthrones.

Homolytic stretching of the sigma and pi frameworks of the diazo moiety in 10-diazoanthrones would lead to a singlet diradical transition state (Fig. 15). The singlet diradical which is formed can be envisioned as having one electron delocalized on the carbon bearing substituent Z as in Eq. 23.
Figure 12: Yukawa-Tsuno plot for decompositions of 2-substituted-10-diazoanthrones in 1-butanol at 90°C.
Figure 13: Yukawa-Tsuno plot for decompositions of 2-substituted-10-diazoanthrones in 1-butanol at 106 °C.
Table 23

<table>
<thead>
<tr>
<th>Z</th>
<th>$E_a$ (kcal)</th>
<th>$\Delta H^\dagger$ (kcal)$^a$</th>
<th>$\Delta S^\dagger$ (e.u.)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>27.7</td>
<td>27.0</td>
<td>+2.5</td>
</tr>
<tr>
<td>Cl</td>
<td>26.5</td>
<td>25.8</td>
<td>-0.2</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>25.4</td>
<td>24.7</td>
<td>-2.4</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>25.1</td>
<td>24.4</td>
<td>-1.8</td>
</tr>
<tr>
<td>CO$_2$CH$_3$</td>
<td>28.9</td>
<td>27.8</td>
<td>+3.3</td>
</tr>
</tbody>
</table>

$^a \Delta H^\dagger = E_a - RT$, $T = 100^\circ C$

$^b \Delta S^\dagger = R \ln \frac{AHN}{RT}$, $T = 100^\circ C$

All substituents Z are known to stabilize formation of 1-substituted-2,4-cyclohexadienyl radicals such as 30.
Figure 14: Arrhenius plot of ln k vs. 1/T for the decompositions of 2-substituted-10-diazomethanes 3-Z in 1-butanol between 90 °C and 106 °C.
Some of the evidence for this is that in which all substituents, regardless of their electronic character, accelerate phenylation of substituted toluenes (Eq. 24, Table 24).\textsuperscript{70}

\begin{table}
\centering
\begin{tabular}{ll}
\hline
\textbf{Z} & \textbf{Total Rate Factor} \\
\hline
H & 1.23\textsuperscript{a} \\
CH\textsubscript{3} & 3.05 \\
Cl & 2.55 \\
Br & 2.15 \\
CO\textsubscript{2}CH\textsubscript{3} & 1.95 \\
NO\textsubscript{2} & 2.31 \\
\hline
\end{tabular}
\caption{Total Rate Factors for Phenylation of \textit{p}-Substituted Toluens in \textit{p}-Dichlorobenzene at 80 °C\textsuperscript{70b}}
\end{table}

Clearly, then, a singlet radical-like transition state is not supported by the present results, since the \(2\text{-CO}_2\text{CH}_3\) substituent decelerates decomposition of \(3\). This is consistent with theory, which predicts the singlet to be a highly energetic state.\(^71\)

The triplet diradical (Fig. 16) is the calculated and observed ground state of 10-anthronylidene\(^71\), but it, too, is discounted as forming in this instance since not only is its generation contradicted by the data, but would also violate spin conservation.

\[ \begin{align*}
\text{3-Z} & \rightarrow \\
& \begin{array}{c}
\text{[O} \quad \text{1} \\
\text{O} \quad \text{1} \\
\text{Z}
\end{array} \\
& \text{[O} \quad \text{1} \\
\text{O} \quad \text{1} \\
\text{Z}
\end{align*} + {^3N_2} \]

**Figure 16:** Homolysis of the diazo moiety of 10-diazoanthrones 3-Z to give triplet 10-anthronylidene and triplet nitrogen.

If a polar, heterolytic transition state is involved, pertinent questions center around the mechanism for nitrogen extrusion. Heterolysis provides either the \(p^2\) singlet 10-anthronylidene or the \(\sigma^2\) singlet (Fig. 17). The \(p^2\) singlet is the calculated lower energy state for cyclohexadienonylidenes.

Linear loss of nitrogen can occur in two ways which are depicted in Fig. 17 to give either carbene. Extrusion of nitrogen from 31 results in \(p^2\) 3a, whose electrons in the \(p\) orbital can be delocalized.
on the carbonyl oxygen. Structure 32 has a very unstable resonance counterpart 33, and is not expected to contribute largely to the

![Chemical structures](image)

**Figure 17:** Possible modes for linear loss of nitrogen in the transition states for decompositions of 3-Z.

The overall electronic structure of 3. Thus, linear decomposition to $\sigma^2$ 3a is considered unlikely to occur.

The $p$-orbital, regardless of which singlet is formed, overlaps the $\pi$-system in 3-Z, and it is the electronic character of the $p$-orbital which determines substituent effects on decomposition. Since the kinetic data support some type of electron-deficient reaction center, linear decomposition to electron-rich $p^2$ 10-anthronylidene is ruled out as a likely mechanism.
Thus, it is concluded that nitrogen is extruded by a non-linear pathway. This mechanism involves major rehybridization of the orbitals around the diazo carbon (Fig. 18). As nitrogen leaves, the sp² and p orbitals combine to form two "sp³-like" orbitals, one electron-poor and one which is electron-rich.

As the process continues toward intermediate formation, the electron-deficient orbital becomes p in character and the electron-sufficient orbital becomes sp². Electron-donors can stabilize the positive "sp³" orbital in the transition state and the ensuing formation of an empty p-orbital, while withdrawing substituents will destabilize both transition state and intermediate. This explanation is the only one which is consistent with the kinetic facts.
It should be noted that the actual electronic structure of carbene 3a may not have an entirely vacant p-orbital, as described in the extreme instance for the \( \sigma^2 \) 10-anthronylidene. Clearly, however, the transition state is electron-deficient, and thus some rehybridization must be occurring.

The present research supports rehybridization in thermal decompositions of diphenyldiazomethanes (Fig. 19). For these molecules, \( \sigma^2 \) diphenylmethylenne is the more stable singlet, and some rehybridization must occur for the energetically favorable carbene to form.

\[
\begin{align*}
\text{W} & \quad \text{S}^- \quad \text{S}^+ \\
\text{C} & \quad \text{N} \equiv \text{N} \\
\text{D} & \\
\end{align*}
\]

\[
\begin{align*}
\Delta & \quad \text{W} \quad \text{S}^+ \quad \text{N}_2^+ \\
\text{D} & \quad \text{C} \quad \text{N}_2^+ \\
\delta^- & \\
\end{align*}
\]

Figure 19: Transition state for non-linear decomposition of substituted diphenyldiazomethanes.

Thus both molecules, 10-diazoanthrone and diphenyldiazomethane, decompose via the same pathway. In diphenyldiazomethane, freely rotating aromatic rings can align to overlap with either an electron-rich or an electron-poor orbital, and consequently, all substituents accelerate decomposition in the system. In 10-diazoanthrones, electronic overlap is only possible with the p-orbital, and only electron-donors stabilize formation of the positive transition state. Hence, the theory of "orbital preference" is supported by the thermal decompositions of substituted 10-diazoanthrones.
5.1 GENERAL TECHNIQUES

Reagents and solvents were obtained commercially and used directly except as otherwise noted.

Melting points were measured with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Infrared spectra were procured on a Perkin-Elmer 457 grating spectrophotometer employing potassium bromide wafers.

High resolution mass spectra were determined utilizing a Kratos MS-30 mass spectrometer.

Proton magnetic resonance spectra were obtained on a Varian EM-390 NMR spectrometer. All samples (unless stated differently) were chloroform-d solutions with tetramethylsilane as an internal standard.

Ultraviolet-visible spectra were recorded in n-butanol employing a Varian DMS 100 UV-Visible spectrophotometer. Molar extinction coefficients and reactant concentrations were determined and kinetic data obtained using a Model 2400 antediluvian Beckman DU spectrophotometer.

Elemental analyses were performed by Microanalysis, Inc., Wilmington, Delaware.
5.2 KINETIC PROCEDURES

For each kinetic run, 1-butanol was distilled at ambient pressure at 116-117 °C and saturated with purified argon. The pure solvent (50 ml) was added to a weighed amount of diazo compound under argon in a 50 ml volumetric flask, and the flask was shaken to dissolve all solid, leaving a yellow solution.

The resulting mixture was pipetted through a glass wool filter into calibrated, matched quartz ultraviolet-visible cells equipped with high-vacuum stopcocks, and cooled to -78 °C in dry ice-acetone. A modified freeze-thaw degassing process was then invoked in the following manner:

Each cell was cooled at -78 °C for 3 min, at which time the stopcock was opened for 2 min. After evacuation of the cell to 0.1 mm Hg, the stopcock was closed and the solution allowed to warm at room temperature for 4.5 min. The cell was heated with a heat gun for 20 sec to increase the vapor pressure of oxygen in the vessel, and then returned to the cooling bath to repeat the cycle. This cooling-warming procedure was performed precisely 6 times. Negligible decomposition of the diazo compounds occurs during this process.

Upon completion of the degassing procedure, thermolyses were carried out by placing the cells in an oil bath thermostatted at the desired temperature with a Sargent-Welch Thermonitor®.

Kinetic data were obtained by following the change in absorbance of a specific solution of diazo compound as a function of time at a wavelength of maximum absorption in the visible spectrum. Cells were
removed at given time intervals to read absorbances. Each cell had to
be removed quickly to the spectrophotometer and washed with toluene to
remove oil from its surfaces before a reading could be taken.
Experiments involving removal of separate cells of the same run at
different time intervals showed that the time spent cooling outside
the constant temperature bath was not a factor in altering rates. All
reactions were followed in excess of two half-lives, and at least 3
runs at different concentrations of 3 cells each were made on each
molecule at 100 °C, while at least 2 runs of 3 cells each at different
concentrations were made at 90 °C and 106 °C.

The absorbances after ten half-lives, A_∞, were found to be
essentially zero in all cases. The starting diazo compound was found
to be completely absent by thin-layer chromatography, indicating no
more than 5% of the starting material remained. Thus, first-order
plots of concentration vs. time were constructed by graphing ln A_t
(absorbance at time t) vs. time (min).

The data for each individual cell in every run were analyzed and
graphed by computer, and the following parameters of every line
calculated: slope (rate-constant), intercept, correlation coefficient,
and half-life. Further, the standard error from regression was
computed for each line. All standard errors fell well below 5% of the
values of the rate constants, and all lines had correlation
coefficients of -0.997 or better.

Overall rate constants for any one compound at a given tempera-
ture are averages of the individual runs. The standard deviations
shown for the average rate constants are standard deviations from the mean. All deviations are close to 5%.

5.3 SYNTHESIS

2-(4-Methylbenzoyl)benzoic acid (9-CH₃): Aluminum chloride (100 g, 0.75 mol, 2 eq.) was added through a Gooch tube to a stirred, ice-cooled suspension of phthalic anhydride (50 g, 0.34 mol) in toluene (300 ml, 353 g, 3.8 mol). After the initial evolution of hydrogen chloride had subsided, the mixture was heated for 45 min to 90 °C, and left to stir for 2.5 h.

The dark-red solution was allowed to cool to room temperature, after which ice was added until the red complex had decomposed and a white slurry remained in its place. Addition of concentrated hydrochloric acid (75 ml) cleared the solution and caused the white solid to descend to the bottom of the flask.

Steam distillation of the excess toluene left a green-brown residue from which the aqueous solution was decanted. The residue was stirred with hot 5% aqueous sodium carbonate (500 ml) for 30 min, and the hot solution was filtered. Acidification of the filtrate afforded the crude product. Recrystallization from benzene/hexane gave 71.5 g (84%) of white needles of 2-(4-methylbenzoyl)benzoic acid (9-CH₃): m.p. 136-138 °C; lit m.p. 138-139 °C; IR (cm⁻¹): 2300-3300, 1700, 1680, 1610, 1580, 1495, 1455, 1425, 1310, 1290, 1285, 1185, 1160, 940, 775, 750, 720; NMR (δ): 2.33 (s, 3H, -CH₃), 7.35 (m, 7H, aromatic), 8.00 (dd, J = 3.0 Hz, J' = 6.0 Hz, 1H, aromatic), 8.89 (s, 1H, -CO₂H).
2-(4-Methoxybenzoyl)benzoic acid (9-OCH₃): Careful addition of aluminum chloride (72 g, 0.59 mol, 3.2 eq.) to a slurry of phthalic anhydride (25 g, 0.17 mol) in anisole (200 ml, 200 g, 1.92 mol) resulted in rapid evolution of hydrogen chloride and formation of a red complex. The mixture was heated slowly to 90 °C and stirred at that temperature for 4 h. Treatment of the reaction product as described in the preparation of 9-CH₃ followed by recrystallization from benzene/hexane yielded 36.5 g (81%) of 2-(4-methoxybenzoyl)benzoic acid (9-OCH₃): m.p. 143-144 °C; lit m.p.⁵⁸ 146 °C; IR (cm⁻¹): 2300-3600, 1690, 1665, 1605, 1585, 1515, 1490, 1460, 1450, 1430, 1420, 1300, 1265, 1185, 1160, 1120, 1090, 1030, 995, 940, 895, 870, 820, 805, 780, 770, 720; NMR (δ): 3.83 (s, 3H, -OCH₃), 6.81 (s, 1H, aromatic), 6.90 (s, 1H, aromatic), 7.46 (m, 5H, aromatic), 8.04 (dd, J = 1.5 Hz, J' = 8.0 Hz, 1H, aromatic), 9.81 (s, 1H, -CO₂H).

2-(4-Chlorobenzoyl)benzoic acid (9-Cl): A mixture of aluminum chloride (50 g, 0.37 mol, 2.1 eq.) and phthalic anhydride (25 g, 0.17 mol) in chlorobenzene (130 ml, 118 g, 1.05 mol) was slowly warmed to 90 °C and stirred for 7 h. Work-up as described in preparation of 9-CH₃ and recrystallization from toluene afforded 38.3 g of white 2-(4-chlorobenzoyl)benzoic acid (9-Cl): m.p. 146-148 °C; lit m.p.⁵⁸ 148-149 °C; IR (cm⁻¹): 2400-3300, 1705, 1690, 1605, 1600, 1585, 1495, 1440, 1410, 1320, 1300, 1270, 1160, 1100, 1025, 940, 860, 830, 790, 775, 720; NMR (δ): 7.28 (m, 3H, aromatic), 7.60 (m, 4H, aromatic), 8.00 (m, 1H, aromatic), 10.09 (s, 1H, -CO₂H).
2-(4-Bromobenzoyl)benzoic acid (9-Br): Phthalic anhydride (25 g, 0.17 mol) was suspended in bromobenzene (150 ml, 224 g, 1.4 mol) and the mixture stirred at room temperature. Aluminum chloride (50 g, 0.37 mol, 2.1 eq) was added to the agitated solution at a rate such that a steady evolution of hydrogen chloride was maintained (about 15 min). The temperature of the red solution was gradually raised to 100 °C and kept there for 7 h.

Treating the reaction product as for 9-CH₃ and recrystallization from toluene left 43.9 g (86%) of white 2-(4-bromobenzoyl)benzoic acid (9-Br): m.p. 164-166 °C; lit m.p. 171-172 °C; IR (cm⁻¹): 2200-3400, 1685, 1595, 1585, 1490, 1485, 1430, 1400, 1310, 1290, 1265, 1155, 1090, 1075, 1015, 935, 890, 850, 820, 780, 750; NMR (δ): 2.05 (sx, d₅-acetone from CO₂H), 7.45 (m, 3H, aromatic), 7.63 (m, 4H, aromatic), 8.06 (m, 1H, aromatic).

2-(4-Methylphenylmethyl)benzoic acid (10-CH₃): Zinc dust (60 g, 0.92 mol) was added slowly to a stirred, ice-cooled suspension of 2-(4-methylbenzoyl)benzoic acid (9-CH₃, 20 g, 0.08 mol) in concentrated ammonium hydroxide (250 ml) and water (100 ml). After all the zinc had been taken up in the suspension, a saturated solution of copper (II) sulfate in concentrated ammonium hydroxide (1 ml) was injected. The reactants were heated slowly to reflux in 3 h and then refluxed for 40 h more.

The hot supernatant liquid was filtered, and the remaining zinc washed with hot 10% aqueous ammonium hydroxide (5 x 50 ml). Acidification of the combined basic extracts and the original filtrate gave
a white precipitate. After filtering and drying the white solid, recrystallization twice from toluene yielded 15.2 g (80%) of 2-(4-methylphenylmethyl)benzoic acid (10-CH₃): m.p. 132-133 °C; lit m.p. 133.5-134 °C; IR (cm⁻¹): 2400-3300, 1670, 1570, 1510, 1485, 1450, 1405, 1310, 1280, 1255, 1145, 1075, 930, 830, 810, 780, 770; NMR (δ): 2.30 (s, 3H, -CH₃), 4.40 (s, 2H, Ar-CH₂-Ar), 7.22 (m, 7H, aromatic), 8.06 (d, J = 7.5 Hz, 1H, aromatic).

2-(4-Methoxyphenylmethyl)benzoic acid (10-OCH₃): 2-(4-Methoxybenzoyl) benzoic acid (9-OCH₃, 5.0 g, 0.02 mol) was dissolved in a mixture of water (100 ml) and concentrated ammonium hydroxide (150 ml). The stirred solution was cooled in ice, and zinc dust (20 g, 0.31 mol) was added in 10 min. A saturated solution of copper (II) sulfate in concentrated ammonium hydroxide (1 ml) was blended into the suspension. The mixture was then refluxed 24 h. Work-up as outlined in the preparation of 10-CH₃ and recrystallization from toluene afforded 4.3 g (91%) of 2-(4-methoxyphenylmethyl) benzoic acid (10-OCH₃): m.p. 114-116 °C; lit m.p. 116-117 °C; IR (cm⁻¹): 2300-3600, 1685, 1620, 1590, 1580, 1520, 1460, 1410, 1320, 1310, 1285, 1260, 1180, 1155, 1110, 1080, 1050, 930, 860, 840, 820, 780, 770, 755; NMR (δ): 3.74 (s, 3H, -OCH₃), 4.33 (s, 2H, Ar-CH₂-Ar), 6.70 (s, 1H, aromatic), 6.80 (s, 1H, aromatic), 7.37 (m, 5H, aromatic), 8.03 (d, J = 6.0 Hz, 1H, aromatic).

2-(4-Chlorophenylmethyl)benzoic acid (10-Cl): 2-(4-Chlorobenzoyl) benzoic acid (9-Cl, 8.0 g, 0.03 mol) was suspended in a mixture of water (100 ml) and concentrated ammonium hydroxide (150 ml). Zinc dust was dropped into the mixture at a rate such that foaming was
avoided. Addition of a saturated copper (II) sulfate/ammonium hydroxide solution (1 ml) to the grey slurry, followed by slow warming to reflux (1 h) cleared the solution, which was then refluxed overnight.

Treatment of the resulting product as described for 10-CH$_3$ provided 6.4 g (84%) of white crystalline 2-(4-chlorophenyl-methyl)benzoic acid (10-Cl): m.p. 129-130 °C; lit m.p.$^{58}$ 131-132 °C; IR (cm$^{-1}$): 2200-3400, 1675, 1595, 1575, 1490, 1450, 1420, 1410, 1320, 1290, 1275, 1260, 1175, 1150, 1110, 1095, 1080, 1055, 1020, 970, 925, 875, 850, 840, 805, 775, 740, 700, 660; NMR (6): 4.40 (s, 2H, Ar-CH$_2$-Ar), 7.17 (m, 7H, aromatic), 8.07 (d, J = 6.0 Hz, 1H, aromatic), 10.71 (s, 1H, -CO$_2$H).

3-(4-Bromophenyl) phthalide (21): Triethylsilane (10.4 g, 14.5 ml. 0.09 mol, 3.0 eq.) was pipetted into a briskly agitated solution of 2-(4-bromobenzoyl)benzoic acid (9-Br, 9.0 g, 0.03 mol) in trifluoroacetic acid (50 ml). The admixture was stirred for 41 h at room temperature.

Vacuum removal of the trifluoroacetic acid and triethylsilane left a white solid, which was washed with 10% aqueous potassium hydroxide (100 ml). The aqueous suspension was extracted with dichloromethane (2 x 75 ml). The combined organic layers were washed with saturated sodium chloride (3 x 50 ml) and dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo, followed by recrystallization of the white solid yielded 6.2 g (74%) of 3-(4-bromophenyl)phthalide (21): m.p. 136-137 °C; lit m.p.$^{58}$
139-140 °C; IR (cm⁻¹): 2930, 1770, 1590, 1475, 1300, 1220, 1115, 1075, 1020, 995, 855, 825, 755; NMR (δ): 6.30 (s, 1H, Ar-CH-O-), 7.41 (m, 7H, aromatic), 8.02 (m, 1H, aromatic).

2-(4-Bromophenylmethyl)benzoic acid (10-Br): 3-(4-Bromophenyl)phthalide (21, 2.0 g, 0.007 mol), red phosphorous (0.16 g, 0.005 mol) and iodine (0.54 g, 0.002 mol) were refluxed 18 h in glacial acetic acid (5 ml) containing water (0.2 ml). The hot reaction mixture, on filtration into 5% aqueous sodium bisulfite (50 ml), precipitated a yellow-white solid (discoloration from iodine) which dissolved upon addition to 10% aqueous sodium carbonate (200 ml).

Filtration of the basic solution and acidification of the filtrate resulted in formation of a white solid, which was extracted into dichloromethane (200 ml), and the organic extracts were dried over magnesium sulfate. Removal of the solvent in vacuo gave 1.8 g (90%) of 2-(4-bromophenylmethyl)benzoic acid (10-Br): m.p. 132-134 °C; lit m.p. 58 133-135 °C; IR (cm⁻¹): 2300-3300, 1680, 1580, 1495, 1415, 1370, 1330, 1315, 1155, 1075, 1020, 930, 840, 780, 740; NMR (δ): 4.39 (s, 2H, Ar-CH₂-Ar), 7.23 (m, 7H, aromatic), 8.07 (dd, J = 1.5 Hz, J' = 6.0 Hz, 1H, aromatic).

2-Methyl-9(10H)-anthracenone (4-CH₃): 2-(4-Methylphenylmethyl) benzoic acid (10-CH₃, 1.6 g, 0.008 mol), was cooled to 0 °C (ice-bath) in a 50-ml Erlenmeyer flask. Concentrated sulfuric acid (5 ml) at 0 °C was added slowly, transforming the white solid into a deep yellow suspension. Allowing the reaction mixture to warm gradually to room
temperature caused dissolution of the remaining solid. After 5 h, the solution had turned to yellow-green.

Pouring the solution over crushed ice afforded a gummy yellow-green substance, which became a granular yellow solid as the ice melted. After the product had been dissolved into dichloromethane (100 ml), the mixture was washed with saturated sodium bicarbonate (3 x 50 ml) and dried over magnesium sulfate. Removal of the solvent in vacuo and recrystallization of the crude product from methanol left 1.2 g (83%) of yellow flocculent needles of 2-methyl-9(10H)-anthracenone (4-CH₃): m.p. 99-100 °C; lit m.p. 99.5-100 °C; IR (cm⁻¹): 3050, 2915, 1655, 1600, 1495, 1480, 1460, 1395, 1390, 1350, 1320, 1300, 1215, 1150, 1095, 1035, 965, 930, 890, 865, 820, 720; NMR (δ): 2.31 (s, 3H, -CH₃), 4.21 (s, 2H, Ar-CH₂-Ar), 7.32 (m, 5H, aromatic), 8.12 (s, 1H, aromatic), 8.30 (m, 1H, aromatic).

2-Methoxy-9(10H)-anthracenone (4-OCH₃): 2-(4-Methoxyphenylmethyl)benzoic acid (10-OCH₃, 4.0 g, 0.02 mol) was added at 0 °C to ice-cooled concentrated sulfuric acid (12 ml). The mixture was left at 0 °C for 2 h, at which time all the solid had dissolved and a dark orange solution remained. Work-up as described for 4-CH₃ and recrystallization from methanol afforded 3.3 g (89%) of yellow 2-methoxy-9(10H)-anthracenone (4-OCH₃): m.p. 98-99 °C; lit m.p. 98-99 °C; IR (cm⁻¹) 2920, 2850, 1650, 1600, 1495, 1460, 1350, 1330, 1305, 1275, 1240, 1150, 1030, 970, 930, 900, 880, 820, 775, 710; NMR (δ): 3.85 (s, 3H, -OCH₃), 4.19 (s, 2H, Ar-CH₂-Ar), 7.32 (m, 5H, aromatic), 7.76 (d, J = 2.5 Hz, 1H, aromatic), 8.32 (m, 1H, aromatic).
2-Chloro-9(10H)-anthracenone (4-Cl): Concentrated sulfuric acid (6 ml) was carefully added to 2-(4-chlorophenylmethyl)benzoic acid (10-Cl, 2.0 g, 0.008 mol) previously cooled to 0 °C. After the mixture had been warmed to room temperature and then stored for 5 h, all solid had dissolved to give a dark yellow-green solution. The mixture was treated in the same manner as for 4-CH₃, and recrystallization from methanol yielded 1.9 g (93%) of 2-chloro-9(10H)-anthracenone (4-Cl): m.p. 153-154 °C; lit m.p.⁵⁸ 156 °C; IR (cm⁻¹): 3070, 2910, 1660, 1610, 1600, 1480, 1465, 1420, 1400, 1360, 1320, 1300, 1260, 1165, 1155, 1085, 965, 930, 900, 860, 820, 720, 685; NMR (δ): 4.20 (s, 2H, Ar-CH₂-Ar), 7.42 (m, 5H, aromatic), 8.18 (d, J = 1.5 Hz, 1H, aromatic), 8.24 (d, J = 4.5 Hz, 1H, aromatic).

2-Bromo-9(10H)-anthracenone (4-Br): Addition of sulfuric acid (4.5 ml) to 2-(4-bromophenylmethyl)benzoic acid (10-Br, 1.5 g, 0.005 mol) previously cooled to 0 °C gave a yellow slurry. After 6 h at room temperature, complete dissolution had occurred, imparting a dark red-brown color to the mixture.

Treatment of the product as described for 4-CH₃ provided 1.4 g (96%) of 2-bromo-9(10H)-anthracenone (4-Br): m.p. 157-159 °C; lit m.p.⁵⁸ 161 °C; IR (cm⁻¹): 2910, 1660, 1595, 1475, 1470, 1420, 1400, 1360, 1320, 1300, 1275, 1170, 1155, 905, 820, 725; NMR (δ): 4.28 (s, 2H, Ar-CH₂-Ar), 7.54 (m, 5H, aromatic), 8.35 (m, 1H, aromatic), 8.47 (d, J = 2.0 Hz, 1H, aromatic).
10-Diazo-2-methyl-9(10H)-anthracenone (3-CH₃): 2 N sodium hydroxide (10 ml, 0.02 mol) was added through a dropping funnel to a stirred solution of 2-methyl-9(10H)-anthracenone (4-CH₃, 1.0 g, 0.005 mol), p-toluenesulfonyl azide (1.0 g, 0.005 mol) and tetra-n-butylammonium bromide (0.05 g, 1.5 x 10⁻⁴ mol) in dichloromethane (150 ml) under oxygen-scrubbed argon. After addition was complete (15 min), the mixture was allowed to stir for 5 h in the dark, at which time the yellow solution had become deep red. The small amount of orange solid in the reaction vessel was filtered. The filtered solution was washed with saturated sodium chloride (3 x 50 ml), dried over magnesium sulfate, and the solvent removed in vacuo to give 0.94 g (84%) of purple-brown 10-diazo-2-methyl-9(10H)-anthracenone (3-CH₃). Purification for kinetic purposes was accomplished by preparative thin-layer chromatography (elution in 10% chloroform/toluene) and recrystallization three times from chloroform/hexane. m.p. 144-145 °C; IR (cm⁻¹): 2925, 2060, 1640, 1625, 1595, 1500, 1485, 1305, 1290, 1210, 1180, 1135, 810, 760, 700; NMR (δ): 2.41 (s, 3H, CH₃), 7.42 (m, 5H, aromatic), 8.21 (d, J = 2 Hz, 1H, aromatic), 8.51 (dd, J = 1 Hz, J' = 75 Hz, 1H, aromatic). UV-Vis (log ε): 417(3.95), 281(4.19), 259(4.20), 242(4.42); MS: 234.0795 (M⁺), 206.0778 (M-N₂), 178.0784 (M-(N₂+ CO)); Anal. Calcd for C₁₅H₁₀N₂O: C, 76.91; H, 4.30 N, 11.96. Found: C, 77.62; H, 4.32; N, 12.17.

10-Diazo-2-methoxy-9(10H)-anthracenone (3-OCH₃): 2-Methoxy-9(10H)-anthracenone (4-OCH₃, 1.0 g, 0.005 mol), p-toluenesulfonyl azide (1.0 g, 0.005 mol) and tetra-n-butylammonium bromide (0.05 g, 1.5 x 10⁻⁴ mol) was added through a dropping funnel to a stirred solution of 2-methoxy-9(10H)-anthracenone (4-OCH₃, 1.0 g, 0.005 mol), p-toluenesulfonyl azide (1.0 g, 0.005 mol) and tetra-n-butylammonium bromide (0.05 g, 1.5 x 10⁻⁴ mol) in dichloromethane (150 ml) under oxygen-scrubbed argon. After addition was complete (15 min), the mixture was allowed to stir for 5 h in the dark, at which time the yellow solution had become deep red. The small amount of orange solid in the reaction vessel was filtered. The filtered solution was washed with saturated sodium chloride (3 x 50 ml), dried over magnesium sulfate, and the solvent removed in vacuo to give 0.94 g (84%) of purple-brown 10-diazo-2-methoxy-9(10H)-anthracenone (3-OCH₃). Purification for kinetic purposes was accomplished by preparative thin-layer chromatography (elution in 10% chloroform/toluene) and recrystallization three times from chloroform/hexane. m.p. 144-145 °C; IR (cm⁻¹): 2925, 2060, 1640, 1625, 1595, 1500, 1485, 1305, 1290, 1210, 1180, 1135, 810, 760, 700; NMR (δ): 2.41 (s, 3H, CH₃), 7.42 (m, 5H, aromatic), 8.21 (d, J = 2 Hz, 1H, aromatic), 8.51 (dd, J = 1 Hz, J' = 75 Hz, 1H, aromatic). UV-Vis (log ε): 417(3.95), 281(4.19), 259(4.20), 242(4.42); MS: 234.0795 (M⁺), 206.0778 (M-N₂), 178.0784 (M-(N₂+ CO)); Anal. Calcd for C₁₅H₁₀N₂O: C, 76.91; H, 4.30 N, 11.96. Found: C, 77.62; H, 4.32; N, 12.17.
mol) were dissolved in dichloromethane (150 ml) which had been saturated with oxygen-scrubbed argon. Dropwise addition of 2 N sodium hydroxide (10 ml, 0.02 mol) over 15 min caused a gradual color change of the solution from yellow to red. Reaction was allowed to proceed in the dark for 5 h. Work-up as described for 3-CH$_3$ afforded 0.85 g (76%) of orange-brown plates of 10-diazo-2-methoxy-9(10H)-anthracenone (3-OCH$_3$): m.p. 132-133 °C; IR (cm$^{-1}$): 3040, 3000, 2940, 2840, 2070, 1640, 1615, 1600, 1505, 1490, 1485, 1370, 1360, 1335, 1310, 1300, 1290, 1240, 1225, 1165, 1140, 1080, 1035, 885, 845, 830, 760; NMR (δ): 3.87 (s, 3H, -OCH$_3$), 7.43 (m, 5H, aromatic), 7.91 (d, J = 1.5 Hz, 1H, aromatic), 8.47 (d, J = 8.5 Hz, 1H, aromatic); UV-Vis (log ε): 427(3.83), 323(3.68), 285(4.04), 248(4.36), 211(3.98); MS: 250.0727 (M$^+$), 222.0689 (M-N$_2$), 194.0714 (M-(N$_2$ + CO)); Anal. Calcd for C$_{15}$H$_{10}$N$_2$O$_2$: C, 72.36; H, 4.07. Found: C, 72.07; H, 4.03.

2-Chloro-10-diazo-9(10H)-anthracenone (3-Cl): Addition of 2 N sodium hydroxide (10 ml, 0.02 mol) to a stirred mixture of 2-chloro-9(10H)-anthracenone (4-Cl, 1.0 g, 0.004 mol), p-toluenesulfonyl azide (1.0 g, 0.05 mol) and tetra-n-butylammonium bromide (0.05 g, 1.5 x 10$^{-4}$ mol) in dichloromethane under purified argon imparted a red color to the solution. The mixture was then stirred in the dark at room temperature for 6 h. Treatment of the product as described for 3-CH$_3$ yielded 0.74 g (66%) of yellow-brown plates of 2-chloro-10-diazo-9(10H)-anthracenone (3-Cl): m.p. 150 °C (dec); IR (cm$^{-1}$): 2060, 1630, 1590, 1475, 1295, 1275, 1160, 820, 805, 750; NMR (δ): 7.41 (m, 5H, aromatic), 8.40 (d, J = 3.0 Hz, 1H, aromatic), 8.51 (d, J = 2.5 Hz,
1H, aromatic); UV-Vis (log e): 417(3.62), 318(3.63), 279(3.89), 258(3.93), 243(4.11), 211(3.93); MS: 254.0228 (M+), 226.0182 (M-N\textsubscript{2}), 198.0222 (M-(N\textsubscript{2} + CO)); Anal. Calcd for C\textsubscript{14}H\textsubscript{7}ClN\textsubscript{2}O: C, 66.03; H, 2.77. Found: C, 65.76; H, 2.82.

10-Diazo-9(10H)-anthracenone (3): 9-(10H)-anthracenone (2.0 g, 0.01 mol), \textit{p}-toluenesulfonyl azide (2.1 g, 0.01 mol) and tetra-n-butyl-ammonium bromide (0.05 g, 1.5 mol) in dichloromethane (150 ml) were treated under purified argon with 10 N sodium hydroxide solution (3 ml, 0.03 mol). The resulting clear red solution was stirred for 4 h. Upon following the procedure outlined for 3-CH\textsubscript{3}, 1.9 g (85%) of red-brown needles of 10-diazo-9(10H)-anthracenone (3) were obtained: m.p. 150 °C (dec); IR (cm\textsuperscript{-1}): 2070, 1645, 1645, 1610, 1595, 1480, 1310, 1300, 1275, 1170, 940, 760; NMR (\textit{d}): 7.38 (m, 6H, aromatic), 8.43 (d, J = 8.5 Hz, 2H, aromatic); MS: 220.0658 (M+), 192.0580 (M-N\textsubscript{2}), 164.0598 (M-(N\textsubscript{2} + CO)).

4-Benzoyl-1,3-benzenedicarboxylic acid (22): Potassium permanganate (95 g, 0.60 mol, 4.9 eq.) was poured slowly into a stirred solution of 2,4-dimethylbenzophenone (25 g, 0.12 mol) in 50% aqueous tert-butanol (500 ml) at room temperature. The mixture was refluxed (5 h) until the purple color disappeared. The manganese dioxide formed was filtered and washed with diethyl ether (3 x 100 ml). The washings were combined with the original filtrate and the aqueous solution was concentrated to one-half volume. Acidification of the remaining warm mixture led to formation of a white precipitate which was filtered and washed with diethyl ether (2 x 50 ml). The remaining solid was
recrystallized from ethanol/water to give 25.9 g (84%) of 4-benzoyl-1,3-benzenedicarboxylic acid (22): m.p. 279-282 °C; lit m.p. 278-280 °C; N.E. Calc = 135.0 g/eq. Found = 138.4 g/eq. IR (cm⁻¹): 2200-3600, 1685, 1595, 1490, 1440, 1410, 1315, 1280, 1250, 1150, 1125, 940, 855, 785, 710; NMR (acetone-d₆, δ): 2.05 (sx, 2H, d₆-acetone from CO₂H), 7.57 (m, 6H, aromatic), 8.37 (dd, J = 3.0 Hz, J' = 9.0 Hz, 1H, aromatic), 8.73 (d, J = 2.0 Hz, 1H, aromatic); MS: 270.0537 (M+).

4-Phenylmethyl-1,3-benzenedicarboxylic acid (23): A mixture of 4-benzoyl-1,3-benzenedicarboxylic acid (22, 15 g, 0.06 mol), zinc dust (40 g, 0.62 mol, 11.3 eq) and a saturated ammoniacal copper (II) sulfate solution (1 ml) in water (100 ml) and concentrated ammonium hydroxide (150 ml) was refluxed for 26 h.

The grey suspension was filtered to give a clear filtrate, and the zinc residue washed with several 50 ml portions of 10% aqueous ammonium hydroxide solution. The basic washings were combined with the primary filtrate, and acidification of the hot, agitated mixture resulted in formation of a white solid. The solution was cooled in ice and filtered. Recrystallization of the white material from ethanol/water yielded 11.0 g (77%) of 4-phenylmethyl-1,3-benzenedicarboxylic acid (23): m.p. 240-242 °C; lit m.p. 242-243 °C; N.E. Calc = 128.0 g/eq. Found = 130.1 g/eq. IR (cm⁻¹): 2200-3500, 1690, 1610, 1595, 1490, 1410, 1260, 1175, 1160, 1135, 1075, 920, 750, 700; NMR (d₆-acetone, δ): 2.05 (sx, 2H, d₆-acetone from -CO₂H), 4.52 (s, 2H, Ar-CH₂-Ar), 7.29 (m, 6H, aromatic), 8.13 (dd, J = 1.5 Hz, J' = 7.5 Hz, 1H, aromatic), 8.61 (d, J = 1.5 Hz, 1H, aromatic); MS: 256.0738 (M+).
9(10H)-Anthracenone-2-carboxylic acid (4-CO₂H): 4-Phenylmethyl-1,3-benzenedicarboxylic acid (23, 3.0 g, 0.01 mol) was treated with cold concentrated sulfuric acid (9 ml) and the resulting green slurry allowed to stand for 5 h at room temperature, at which time all solid had dissolved.

The dark green mixture was added to ice, forming a green gum which was slowly transformed by stirring into a yellow granular substance. As the product 9(10H)-anthracenone-2-carboxylic acid (4-CO₂H) was only sparingly soluble in a variety of hot solvents, recrystallization was difficult and the crude solid (2.7 g, 97%) was deemed sufficient for subsequent use. m.p. > 300 °C; IR(cm⁻¹): 2400-3500, 1695, 1660, 1610, 1460, 1420, 1395, 1295, 1260, 1135, 1090, 980, 925, 715; MS: 238.0624 (M⁺), 193.0645 (M-CO₂H), 165.0698 (M-(CO₂H + CO)).

Methyl 9(10H)-anthracenone-2-carboxylate (4-CO₂Me): 9(10H)-Anthracenone-2-carboxylic acid (4-CO₂H, 0.6 g, 0.003 mol) was refluxed in argon-saturated methanol (200 ml) for 4.5 h, at which time all solid had disappeared and a yellow solution remained. Thin-layer chromatography analysis indicated the absence of starting material. Addition of the solution to water (200 ml) resulted in a yellow slurry, which was extracted with diethyl ether (3 x 75 ml). The combined organic layers were washed with saturated sodium bicarbonate (3 x 75 ml), dried over sodium sulfate, and the solvent removed in vacuo to yield 0.55 g of a yellow-orange solid showing three spots by
thin-layer chromatography. Elution of a silica gel column with 50% hexane/chloroform effected separation to give 0.27 g (43%) of methyl 9(10H)-anthracenone-2-carboxylate (4-CO_2Me): m.p. 136-137 °C; IR (cm⁻¹): 2910, 1720, 1660, 1430, 1390, 1315, 1280, 1250, 1120, 1090, 715, 695; NMR (δ): 3.93 (s, 3H, CO_2CH_3), 4.28 (s, 2H, Ar-CH₂-Ar), 7.33 (m, 5H, aromatic), 8.16 (m, 2H, aromatic); MS: 252.0799 (M+).

Methyl 10-diazo-9(10H)-anthracenone-2-carboxylate (3-CO_2Me): A solution of sodium carbonate (0.3 g, 0.003 mol, 2.2 eq) in water (5 ml) was introduced into a mixture of methyl 9(10H)-anthracenone-2-carboxylate (4-CO_2Me, 0.35 g, 0.001 mol), p-toluenesulfonyl azide (0.3 g, 0.0015 mol) and tetra-n-butyl ammonium bromide (0.05 g, 1.5 x 10⁻⁴ mol) in argon-saturated dichloromethane (150 ml). The resultant solution turned dark red upon stirring in the dark for 5 h. The organic solution was filtered, washed with saturated sodium bicarbonate (3 x 50 ml), dried over magnesium sulfate, and the solvent removed in vacuo to give 0.32 g (83%) of brown plates of methyl 10-diazo-9(10H)-anthracenone-2-carboxylate (4-CO_2Me) which decomposed at 150 °C before melting. Kinetic purity was obtained via preparative thin-layer chromatography (2% acetone/chloroform); IR (cm⁻¹): 2920, 2075, 1720, 1640, 1600, 1490, 1435, 1295, 1250, 1165, 1145, 1110, 760, 700; NMR (δ): 3.95 (s, 3H, CO_2CH_3), 7.48 (m, 4H, aromatic), 8.29 (dd, J = 3.0 Hz, J' = 9.0 Hz, 1H, aromatic), 8.50 (dd, J = 1.5 Hz, J' = 7.5 Hz, 1H, aromatic), 9.12 (d, J = 3.0 Hz, 1H, aromatic); UV-Vis (log ε): 406(3.58), 341(3.68), 311(3.63), 274(3.88), 246(3.99), 220(3.92); MS:
278.0692 (M+), 250.0589 (M-N2), 222.0576 (M-N2 + CO); Anal. Calcd for C16H10N2O3: C, 68.91; H, 3.44. Found: C, 69.13; H, 3.63.

2-Methyl-5-nitrobenzonitrile (12): 2-Methyl-5-nitrobenzonitrile was prepared by adapting the methodology of Friedman and Shechter.59a (The nitronitrile had been produced previously only via nitration of o-tolunitril.60) 2-Bromo-4-nitrotoluene (15 g, 0.07 mol) was heated in refluxing dimethylformamide (20 ml) for 3 h with copper (I) cyanide (7.8 g, 0.09 mol). The mixture was then poured into water (100 ml) and stirred for 10 min.

The nitrile-cuprous cyanide complex was filtered and destroyed by stirring with 30% aqueous sodium cyanide (100 ml) for 20 min. The free nitrile was extracted into benzene (3 x 100 ml) and the organic layer filtered to remove copper metal. Washing of the benzene solution with water (3 x 50 ml), drying over magnesium sulfate, and removal of the solvent in vacuo yielded a crude orange-brown product which was boiled with activated charcoal and recrystallized from 95% ethanol to give 8.2 g (71%) of dark-brown 2-methyl-5-nitrobenzonitrile (12): m.p. 102-104 °C; lit m.p.59b 106-108 °C; IR (cm⁻¹): 3100, 3080, 2930, 2870, 2240, 1625, 1580, 1525, 1480, 1440, 1385, 1355, 1310, 1275, 1140, 1085, 1035, 925, 845, 810, 750, 735; NMR (δ): 2.63 (s, 3H, -CH3), 7.47 (d, J = 8.5 Hz, 1H, aromatic), 8.27 (dd, J = 2.5 Hz, J' = 9.0 Hz, 1H, aromatic); MS: 162.0391 (M+), 116.0466 (M-NO2)

2-Methyl-5-nitrobenzoic acid (13): Addition of 70% concentrated sulfuric acid to 2-methyl-5-nitrobenzonitrile (12, 9.0 g, 0.06 mol) resulted in an immediate temperature increase. The mixture was heated...
slowly to 175 °C in 1 h (dissolution occurred between 120 and 150 °C) during which time the solution darkened. Continued heating at 175 °C for 45 min caused formation of white crystals in the condenser, at which time analysis by thin-layer chromatography showed an absence of starting material. The reaction solution was cooled to room temperature and poured over ice (200 ml).

Suction filtration of the suspension left a dark solid which provided a dark red solution when dissolved in 10% sodium hydroxide (100 ml). The aqueous mixture was boiled with activated charcoal, filtered, and acidified with hydrochloric acid to give a tan solid which was taken up in diethyl ether (200 ml). The ethereal solution was washed with saturated sodium chloride (3 x 75 ml); drying over magnesium sulfate and removal of the solvent in vacuo yielded the crude acid. Recrystallization from 95% ethanol afforded 5.5 g (55%) of white crystals of 2-methyl-5-nitrobenzoic acid (13): m.p. 176-178 °C; lit m.p. 179 °C; IR (cm⁻¹): 2300-3600, 1695, 1615, 1520, 1450, 1415, 1350, 1335, 1280, 1260, 1185, 1135, 925, 915, 850, 820, 740, 690; NMR (d₆-acetone, δ): 2.05 (sx, 1H, d₅-acetone from -CO₂H), 2.72 (s, 3H, -CH₃), 7.57 (d, J = 9.0 Hz, 1H, aromatic), 8.27 (dd, J = 3.0 Hz, J' = 8.5 Hz, 1H, aromatic), 8.70 (d, J = 3.0 Hz, 1H, aromatic); MS: 181.0358 (M⁺), 163.0259 (M-H₂O), 135.0374 (M-NO₂).

2-Methyl-5-nitrobenzophenone (14): 2-Methyl-5-nitrobenzoic acid (13, 4.0 g, 0.02 mol) and thionyl chloride (15 ml, 24.4 g, 0.21 mol) were heated at reflux (1 h) until the mixture became clear yellow. Distillation of the excess thionyl chloride left behind red-brown
2-methyl-5-nitrobenzoyl chloride (m.p. 59 °C; lit m.p. 61 59 °C). The remaining solid was dissolved in benzene (40 ml) and aluminum chloride (6.2 g, 0.05 mol) was added slowly to the solution. The reaction mixture was heated to 40 °C and the temperature maintained between 30 °C and 40 °C for 2.5 h.

Treatment of the solution with ice and hydrochloric acid gave two layers. The organic layer was decanted and washed with saturated sodium bicarbonate (3 x 50 ml) and dried over magnesium sulfate. Removal of the solvent in vacuo and subsequent recrystallization from ethanol/water yielded 4.1 g (77%) of 2-methyl-5-nitrobenzophenone (14): m.p. 77-79 °C; lit m.p. 61 79 °C; IR (cm⁻¹): 3080, 2960, 1670, 1605, 1535, 1460, 1365, 1295, 1180, 985, 890, 875, 815, 760, 725, 665; NMR (δ): 2.43 (s, 3H, -CH₃), 7.51 (m, 4H, aromatic), 7.81 (m, 2H, aromatic), 8.20 (m, 2H, aromatic).
APPENDIX

Kinetic Data for Selected Thermal Decompositions of
10-Diazoanthrones in 1-Butanol at 100 °C
2-Methyl-10-diazoanthrone

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>A</th>
<th>ln A</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.761</td>
<td>-.2731</td>
</tr>
<tr>
<td>61</td>
<td>0.712</td>
<td>-.3397</td>
</tr>
<tr>
<td>90</td>
<td>0.663</td>
<td>-.4109</td>
</tr>
<tr>
<td>120</td>
<td>0.622</td>
<td>-.4748</td>
</tr>
<tr>
<td>150</td>
<td>0.581</td>
<td>-.5430</td>
</tr>
<tr>
<td>180</td>
<td>0.539</td>
<td>-.6180</td>
</tr>
<tr>
<td>210</td>
<td>0.498</td>
<td>-.6971</td>
</tr>
<tr>
<td>241</td>
<td>0.459</td>
<td>-.7787</td>
</tr>
<tr>
<td>270</td>
<td>0.434</td>
<td>-.8347</td>
</tr>
<tr>
<td>300</td>
<td>0.407</td>
<td>-.8989</td>
</tr>
<tr>
<td>331</td>
<td>0.374</td>
<td>-.9835</td>
</tr>
<tr>
<td>362</td>
<td>0.350</td>
<td>-1.050</td>
</tr>
<tr>
<td>390</td>
<td>0.339</td>
<td>-1.082</td>
</tr>
<tr>
<td>452</td>
<td>0.271</td>
<td>-1.306</td>
</tr>
<tr>
<td>480</td>
<td>0.253</td>
<td>-1.374</td>
</tr>
<tr>
<td>511</td>
<td>0.237</td>
<td>-1.440</td>
</tr>
<tr>
<td>540</td>
<td>0.219</td>
<td>-1.519</td>
</tr>
<tr>
<td>570</td>
<td>0.207</td>
<td>-1.575</td>
</tr>
</tbody>
</table>

\[ k_{obs} = 2.44 \pm 0.012a \times 10^{-3} \text{ min}^{-1} \]

\[ a \text{Standard error for line} \]
Figure 20. Graphical analysis of the thermal decomposition of 2-Methyl-10-diazoanthrone at 100 °C.
2-Methoxy-10-diazoanthrone 425 nm 100 °C

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>A</th>
<th>ln A</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>0.533</td>
<td>-0.6292</td>
</tr>
<tr>
<td>43</td>
<td>0.489</td>
<td>-0.7154</td>
</tr>
<tr>
<td>62</td>
<td>0.428</td>
<td>-0.8486</td>
</tr>
<tr>
<td>83</td>
<td>0.383</td>
<td>-0.9597</td>
</tr>
<tr>
<td>102</td>
<td>0.352</td>
<td>-1.044</td>
</tr>
<tr>
<td>122</td>
<td>0.315</td>
<td>-1.155</td>
</tr>
<tr>
<td>143</td>
<td>0.282</td>
<td>-1.266</td>
</tr>
<tr>
<td>162</td>
<td>0.256</td>
<td>-1.363</td>
</tr>
<tr>
<td>182</td>
<td>0.226</td>
<td>-1.487</td>
</tr>
<tr>
<td>202</td>
<td>0.204</td>
<td>-1.590</td>
</tr>
<tr>
<td>222</td>
<td>0.182</td>
<td>-1.704</td>
</tr>
<tr>
<td>242</td>
<td>0.163</td>
<td>-1.814</td>
</tr>
<tr>
<td>262</td>
<td>0.146</td>
<td>-1.924</td>
</tr>
<tr>
<td>282</td>
<td>0.134</td>
<td>-2.010</td>
</tr>
<tr>
<td>325</td>
<td>0.104</td>
<td>-2.263</td>
</tr>
</tbody>
</table>

\( k_{obs} = 5.43 \pm 0.013 \times 10^{-3} \text{ min}^{-1} \)

\( t_{1/2} = 128 \text{ min} \)
Figure 21. Graphical analysis of the thermal decomposition of 2-methoxy-10-diazoanthrone at 100 °C.
**2-Chloro-10-diazoanthrone**  

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>A</th>
<th>ln A</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>0.728</td>
<td>-0.3174</td>
</tr>
<tr>
<td>64</td>
<td>0.692</td>
<td>-0.3682</td>
</tr>
<tr>
<td>98</td>
<td>0.661</td>
<td>-0.4140</td>
</tr>
<tr>
<td>125</td>
<td>0.622</td>
<td>-0.4748</td>
</tr>
<tr>
<td>154</td>
<td>0.591</td>
<td>-0.5259</td>
</tr>
<tr>
<td>184</td>
<td>0.552</td>
<td>-0.5942</td>
</tr>
<tr>
<td>214</td>
<td>0.528</td>
<td>-0.6389</td>
</tr>
<tr>
<td>244</td>
<td>0.497</td>
<td>-0.6992</td>
</tr>
<tr>
<td>274</td>
<td>0.467</td>
<td>-0.7614</td>
</tr>
<tr>
<td>304</td>
<td>0.453</td>
<td>-0.7919</td>
</tr>
<tr>
<td>334</td>
<td>0.429</td>
<td>-0.8463</td>
</tr>
<tr>
<td>364</td>
<td>0.407</td>
<td>-0.8989</td>
</tr>
<tr>
<td>394</td>
<td>0.375</td>
<td>-0.9808</td>
</tr>
<tr>
<td>424</td>
<td>0.356</td>
<td>-1.033</td>
</tr>
<tr>
<td>456</td>
<td>0.342</td>
<td>-1.073</td>
</tr>
<tr>
<td>485</td>
<td>0.328</td>
<td>-1.115</td>
</tr>
<tr>
<td>514</td>
<td>0.307</td>
<td>-1.181</td>
</tr>
<tr>
<td>547</td>
<td>0.274</td>
<td>-1.295</td>
</tr>
<tr>
<td>694</td>
<td>0.217</td>
<td>-1.528</td>
</tr>
<tr>
<td>724</td>
<td>0.208</td>
<td>-1.570</td>
</tr>
<tr>
<td>754</td>
<td>0.197</td>
<td>-1.625</td>
</tr>
<tr>
<td>784</td>
<td>0.188</td>
<td>-1.671</td>
</tr>
<tr>
<td>812</td>
<td>0.178</td>
<td>-1.726</td>
</tr>
<tr>
<td>842</td>
<td>0.171</td>
<td>-1.766</td>
</tr>
</tbody>
</table>

$k_{obs} = 1.82 \pm 0.041 \times 10^{-3} \text{ min}^{-1}$

$t_{1/2} = 381 \text{ min}$
Figure 22. Graphical analysis of the thermal decomposition of 2-chloro-10-diazoanthrone at 100 °C.
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>A</th>
<th>ln A</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.771</td>
<td>-.2601</td>
</tr>
<tr>
<td>120</td>
<td>0.741</td>
<td>-.2998</td>
</tr>
<tr>
<td>180</td>
<td>0.714</td>
<td>-.3369</td>
</tr>
<tr>
<td>270</td>
<td>0.669</td>
<td>-.4019</td>
</tr>
<tr>
<td>360</td>
<td>0.633</td>
<td>-.4573</td>
</tr>
<tr>
<td>450</td>
<td>0.596</td>
<td>-.5175</td>
</tr>
<tr>
<td>540</td>
<td>0.562</td>
<td>-.5763</td>
</tr>
<tr>
<td>630</td>
<td>0.528</td>
<td>-.6387</td>
</tr>
<tr>
<td>720</td>
<td>0.497</td>
<td>-.6992</td>
</tr>
<tr>
<td>810</td>
<td>0.466</td>
<td>-.7636</td>
</tr>
<tr>
<td>900</td>
<td>0.439</td>
<td>-.8233</td>
</tr>
<tr>
<td>990</td>
<td>0.415</td>
<td>-.8795</td>
</tr>
<tr>
<td>1080</td>
<td>0.391</td>
<td>-.9390</td>
</tr>
<tr>
<td>1200</td>
<td>0.359</td>
<td>-1.024</td>
</tr>
<tr>
<td>1320</td>
<td>0.335</td>
<td>-1.094</td>
</tr>
<tr>
<td>1440</td>
<td>0.307</td>
<td>-1.181</td>
</tr>
<tr>
<td>1560</td>
<td>0.282</td>
<td>-1.265</td>
</tr>
<tr>
<td>1680</td>
<td>0.261</td>
<td>-1.343</td>
</tr>
<tr>
<td>1800</td>
<td>0.241</td>
<td>-1.423</td>
</tr>
<tr>
<td>1920</td>
<td>0.224</td>
<td>-1.496</td>
</tr>
<tr>
<td>2040</td>
<td>0.206</td>
<td>-1.580</td>
</tr>
<tr>
<td>2160</td>
<td>0.191</td>
<td>-1.655</td>
</tr>
</tbody>
</table>

$k_{obs} = 0.668 \pm 0.001 \times 10^{-3} \text{ min}^{-1}$

$t_{1/2} = 1040 \text{ min}$
Figure 23. Graphical analysis of the thermal decomposition of methyl 10-diazo-anthrone-2-carboxylate at 100 °C.
10-Diazoanthrone

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>A</th>
<th>ln A</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.513</td>
<td>-0.6674</td>
</tr>
<tr>
<td>90</td>
<td>0.492</td>
<td>-0.7083</td>
</tr>
<tr>
<td>120</td>
<td>0.473</td>
<td>-0.7491</td>
</tr>
<tr>
<td>150</td>
<td>0.454</td>
<td>-0.7900</td>
</tr>
<tr>
<td>180</td>
<td>0.436</td>
<td>-0.8309</td>
</tr>
<tr>
<td>210</td>
<td>0.418</td>
<td>-0.8717</td>
</tr>
<tr>
<td>240</td>
<td>0.401</td>
<td>-0.9126</td>
</tr>
<tr>
<td>270</td>
<td>0.385</td>
<td>-0.9535</td>
</tr>
<tr>
<td>300</td>
<td>0.370</td>
<td>-0.9943</td>
</tr>
<tr>
<td>333</td>
<td>0.354</td>
<td>-1.039</td>
</tr>
<tr>
<td>361</td>
<td>0.341</td>
<td>-1.077</td>
</tr>
<tr>
<td>390</td>
<td>0.327</td>
<td>-1.117</td>
</tr>
<tr>
<td>420</td>
<td>0.314</td>
<td>-1.158</td>
</tr>
<tr>
<td>480</td>
<td>0.289</td>
<td>-1.240</td>
</tr>
<tr>
<td>510</td>
<td>0.278</td>
<td>-1.280</td>
</tr>
<tr>
<td>540</td>
<td>0.267</td>
<td>-1.321</td>
</tr>
<tr>
<td>570</td>
<td>0.256</td>
<td>-1.362</td>
</tr>
<tr>
<td>603</td>
<td>0.245</td>
<td>-1.407</td>
</tr>
<tr>
<td>630</td>
<td>0.236</td>
<td>-1.444</td>
</tr>
<tr>
<td>660</td>
<td>0.227</td>
<td>-1.485</td>
</tr>
<tr>
<td>750</td>
<td>0.200</td>
<td>-1.607</td>
</tr>
<tr>
<td>780</td>
<td>0.192</td>
<td>-1.648</td>
</tr>
<tr>
<td>810</td>
<td>0.185</td>
<td>-1.689</td>
</tr>
<tr>
<td>840</td>
<td>0.177</td>
<td>-1.730</td>
</tr>
<tr>
<td>900</td>
<td>0.169</td>
<td>-1.778</td>
</tr>
<tr>
<td>960</td>
<td>0.154</td>
<td>-1.871</td>
</tr>
<tr>
<td>1020</td>
<td>0.140</td>
<td>-1.966</td>
</tr>
<tr>
<td>1050</td>
<td>0.134</td>
<td>-2.009</td>
</tr>
</tbody>
</table>

\[ k_{obs} = 1.36 \pm 0.004 \times 10^{-3} \text{ min}^{-1} \]

\[ t_{1/2} = 509 \text{ min} \]
Figure 24. Graphical analysis for the thermal decomposition of 10-diazoanthrone at 100 °C.
REFERENCES


71. Ref. 8, pp. 200-203.