THERMAL AND MASS SPECTRAL FRAGMENTATION OF

2,5-DIPHENYL-3,4-DIAZACYCLOPENTADIENONE-3,4-DIOXIDE

by

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ABSTRACT

Orbital symmetry considerations suggest that cheletropic fragmentation of 2,5-diphenyl-3,4-diazacyclopentadienone-3,4-dioxide (5) along the thermally allowed $[\sigma^2 s + \sigma^2 s + \sigma^2 a + \omega^2 s]$ pathway would yield benzonitrile oxide and carbon monoxide as primary products. However, experiments show that benzonitrile and carbon dioxide are the major products in solid phase and dilute solution pyrolyses of 5 in complete agreement with its mass spectral fragmentation. Benzonitrile oxide and carbon monoxide are produced, but the major reaction pathway is not the postulated cheletropic fragmentation. The rate of disappearance of 5 during dilute solution pyrolysis is first order in [5]; $k = 2.08 \times 10^{-4} \sec^{-1}$ (157-58°), $\Delta G^{\ddagger} = 32.7$ k-cal/mole. A scheme is proposed which accounts for the formation of the major products in the thermal and mass spectral fragmentation of 5, and the mass spectrum of 2,5-dicarbomethoxy-3,4-diazacyclopentadienone-3,4-dioxide is discussed.

Total π bond orders calculated by the simple HMO method are discussed as a means of predicting mass spectral fragmentation and correlation of mass spectral and thermal processes for the compounds examined.

An unsuccessful attempt to synthesize 3,4-diazacyclopentadienone-3,4-dioxide is described.

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I gratefully acknowledge a sample of authentic tribenzamide supplied by Dr. Edwin M. Kaiser of the University of Missouri.

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INTRODUCTION

The 3,4-diazacyclopentadienone-3,4-dioxides (1) comprise a novel class of heterocyclic compounds whose structures have only recently been established.[1]

(2, $R_1 = R_2 = H$)

1
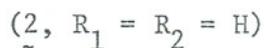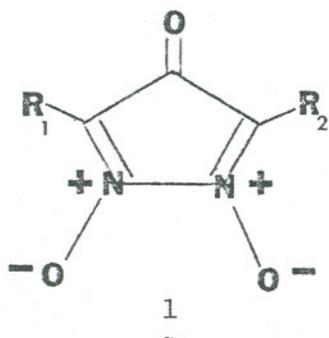
Known derivatives of the ring system are brilliantly colored, generally high melting, crystalline solids.[1] The compounds possess some quite interesting spectral properties most noteworthy of which is the appearance of the carbonyl absorption band at approximately 1640 cm^{-1} in the infrared spectrum.[1]

Recent work by Freeman and Hoare[2] has demonstrated that 2,5-disubstituted-3,4-diazacyclopentadienone-3,4-dioxides are potent 1,3 dipoles capable of forming cycloadducts with such dipolarophiles as acrylonitrile, methyl acrylate and butyl vinyl ether. These cyclo-additions are exemplified by equation 1. Diaryl and dialkyl as well as alkyl aryl derivatives of 1 are known.[1]

$$CH_2C{\equiv}CHX$$

1

1   3   4

1
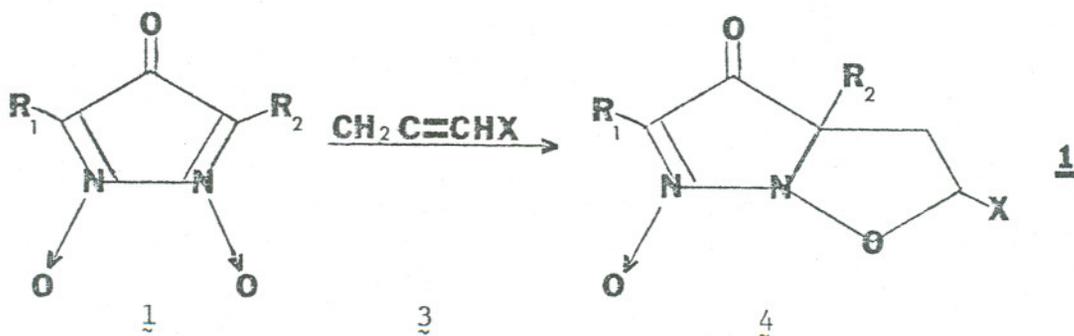
The structure of 1 suggests that it might be capable of fragmenting to produce nitrile oxides and carbon monoxide, and inspection of the basis set orbitals available to the molecule reveals that such a thermally allowed $[\sigma^2 s + \sigma^2 s + \sigma^2 a + \omega^2 s]$ cheletropic fragmentation pathway is available. Therefore, pyrolysis of derivatives of 1 might provide an interesting new means for the generation of nitrile oxides, which are interesting and synthetically useful[4] 1,3 dipoles. Part one of this thesis describes the pyrolytic fragmentation of 2,5-diphenyl-3,4-diazacyclopentadienone-3,4-dioxide (5), and compares it with the electron impact induced fragmentation of the compound. The mass spectrum of the 2,5-dicarbomethoxy derivative of 1 is also discussed.

Part two of this thesis describes an attempted synthesis of the as yet unknown 3,4-diazacyclopentadienone-3,4-dioxide (2).

DISCUSSION PART ONE

Our initial interest in carrying out pyrolysis studies on 3,4-diazacyclopentadienone derivatives arose from the speculation that one might be able to bring about the fragmentation of the molecule to produce carbon monoxide and nitrile oxides possibly in concerted fashion. Such a reaction would constitute a thermally allowed $[\sigma^2 s + \sigma^2 s + \sigma^2 a + \omega^2 s]$ cheletropic fragmentation[3] as shown in equation 2.
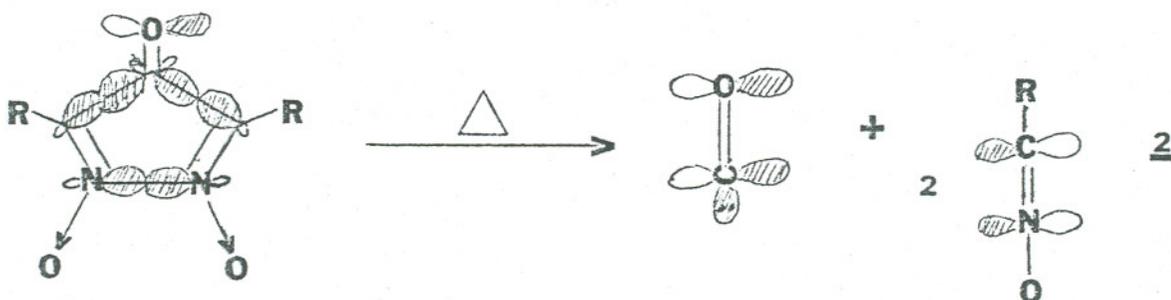
Studies were carried out on the diphenyl derivative (5) since it is quite readily synthesized.[1] Furthermore, benzonitrile oxide, its dimer, and many of its 1,3 cycloaddition products are well characterized.[4]

5
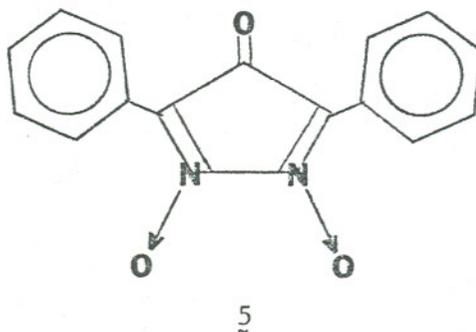
Compound 5 was synthesized according to the method of Freeman et. al.[1] by treating a solution of 1,3 diphenylacetone in acetic acid-ethanol with sodium nitrite over a period of one week. The product, which crystallized from the reaction mixture, was filtered, washed with ethanol-water, dried in air and used without further purification in all subsequent operations.

Initial pyrolyses were fusions carried out on a small scale. Approximately 0.1 g of 5 was heated (190-200°) to form a red melt which degassed explosively at about 196°. An infrared spectrum of the resulting pyrolysate displayed a nitrile band.[5] Preparative thin layer chromatography revealed the pyrolysate to be a complex mixture having at least sixteen constituents. Two compounds (6 and 7) were characterized, the structures of which shed some light on the fate of the starting material. 2,4,6-Triphenyl-1,3,5-triazine (6)[6] is a well known trimer of benzonitrile.[6] Isolation of 6 coupled with the presence of the nitrile band in the infrared spectrum of the crude pyrolysate is a strong indication that benzonitrile is formed in the reaction. Formation of the second compound 3,5-diphenyl-1,2,4-oxadiazole (7)[7,8,9] probably occurred through cycloaddition of benzonitrile oxide to benzonitrile. The oxadiazole (7) is in fact the only cycloadduct isolated when authentic benzonitrile oxide reacts with benzonitrile.[4]

6

7
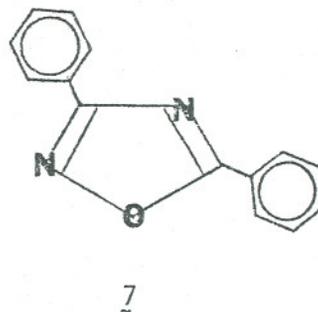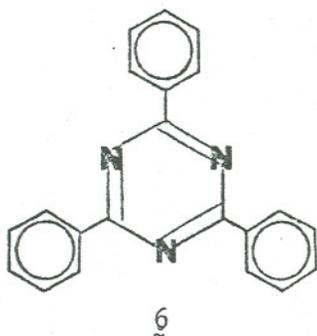
Formation of benzonitrile indicates that an oxygen atom bound to nitrogen in 5 is removed from nitrogen in some way. We postulate that this oxygen is expelled in a molecule of carbon dioxide as shown in Scheme I.

In order to determine what gases were produced in the pyrolysis, we performed a mass spectral analysis on the gas mixture formed during pyrolysis of 5. The experiment was carried out by pyrolyzing crystalline 5 in an evacuated ($P = 10^{-6}$ micron) tube which could be attached to the gas inlet system of the mass spectrometer. Results are shown in Table I.

Table I

Gases produced by pyrolysis of 5 as determined by mass spectrometry.

Gases*	Mole%
CO_2	60
N_2O	4
NO	13
N_2	11
CO	12

* Nitrogen and nitrous oxide were confirmed by peak enhancement using authentic samples. Exact masses of the other three gases were determined by peak matching to nitrogen and nitrous oxide.

An infrared spectrum of the oil remaining in the pyrolysis tube revealed, in addition to the expected nitrile band, an isocyanate band.[5] Subsequent experiments showed the oil to be a mixture consisting of benzonitrile (74 mole%) and phenyl isocyanate (26 mole%).

In further studies, we ascertained that benzonitrile and carbon dioxide are produced in equimolar amounts on pyrolysis of dilute (0.04 M) solutions of 5 in bromobenzene and in diglyme. Furthermore, the amounts of carbon dioxide and of benzonitrile produced in such pyrolyses are one half molar equivalent based on starting material 5. We also found that there is essentially no pyrolysis under these conditions unless the reflux temperature of the solvent used is substantially above 110°.

In addition to benzonitrile, phenyl isocyanate, and the gases shown in Table I, dilute solution pyrolysis of 5 produced a complex mixture of twenty or more compounds. One of these compounds is tribenzamide (8).[10,11] It should be noted that the dimer of benzonitrile oxide, diphenylfuroxane (9)[4,12] has not been detected by us under any conditions.
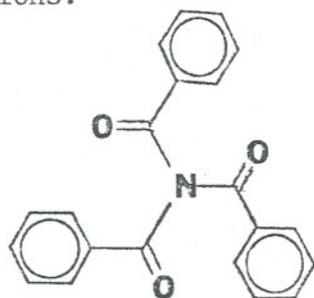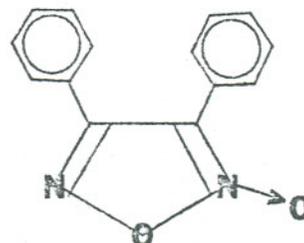
8   9

We have found benzonitrile and carbon dioxide to be products in both solid phase and dilute solution pyrolyses which strongly suggests that the major reaction pathway is unimolecular. However, this interpretation is not unambiguously established by our results.

One may account for formation of the major products, and secondary products arising from them with Scheme I.

As required by Scheme I, the rate of disappearance of 5 during pyrolysis in dilute solution is first order in [5]. Thus, compound 5 was dissolved in bromobenzene to give 7×10^{-4} M and 7×10^{-2} M solutions which were brought to reflux, and aliquots of each were periodically withdrawn and brought to room temperature. The absorbance of each aliquot at 466 nm was measured. A plot of log absorbance versus time gave a straight line for more than three half lives ($t_{1/2}$ = 55 min). The first order rate constant evaluated for each of the above pyrolyses was $k = 2 \times 10^{-4} \text{sec}^{-1}$ at 157-58°. The free energy of activation for the reaction is $\Delta G^{\ddagger}$ = 32.7 k-cal/mole.
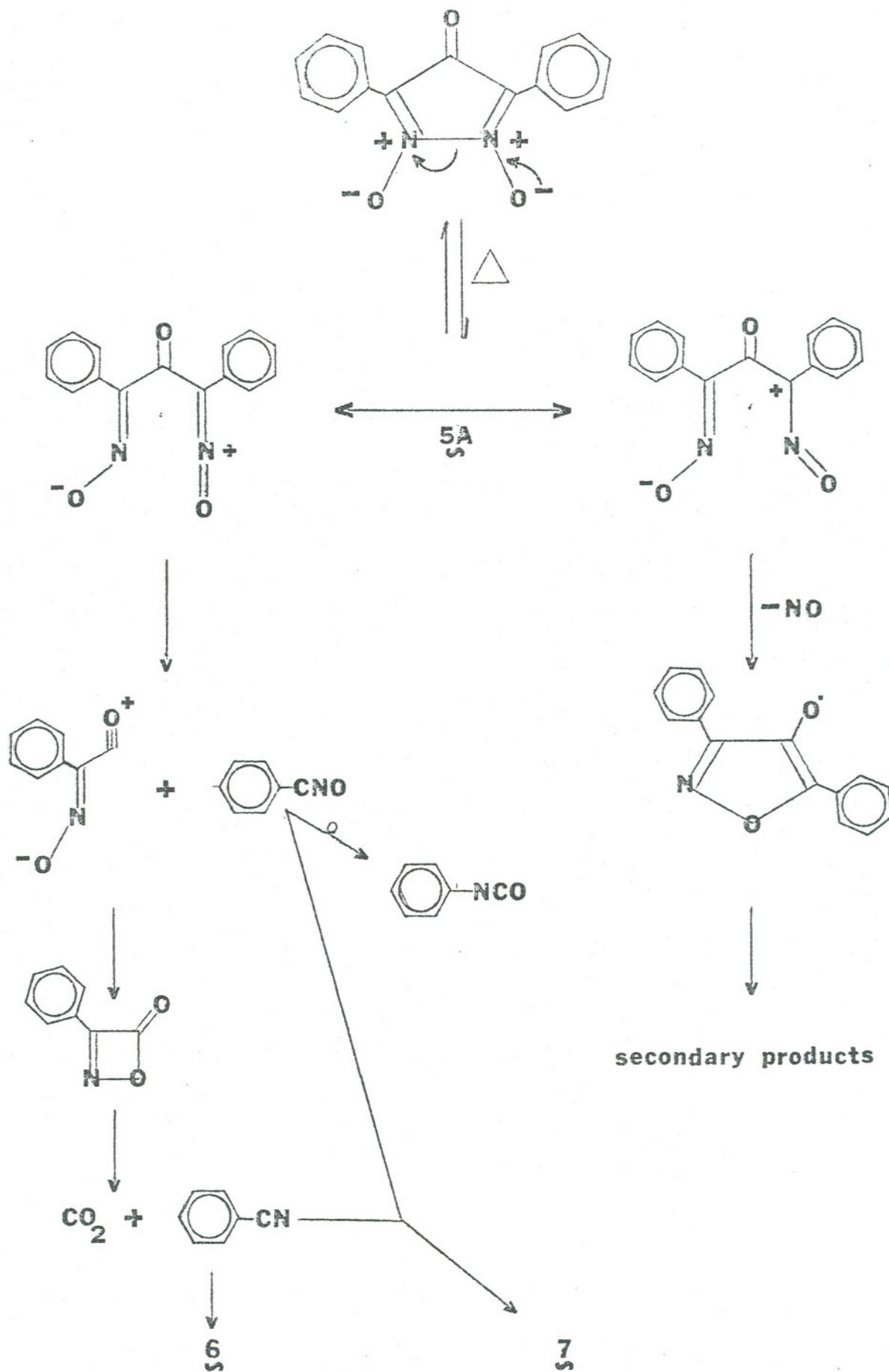
Scheme I thermal fragmentation of 5.

The thermal fragmentation suggested in Scheme I accounts for most of the observed phenomena. The scheme postulates that at the temperature of refluxing bromobenzene, compound 5 is in equilibrium with the resonance stabilized ring opened form 5A. The scheme further postulates that reclosure of the N-N bond (5A → 5) must compete with two other available reaction paths. The first is cleavage of the bond α to the carbonyl to yield a molecule of benzonitrile oxide and what is, at least formally, an alpha nitrosoketene. This intermediate may then cyclize to yield a highly reactive β-azalactone which fragments to yield carbon dioxide and benzonitrile. The second path is attack by nitrogen-bound oxygen at the positive center adjacent to the carbonyl in 5A to yield a 5-nitrosoisoxazoline which loses nitrogen monoxide to yield a resonance stabilized 4-oxo-3,5-diphenylisoxazolyl radical. This radical then reacts to form secondary products.

The secondary products 2,4,6-triphenyl-1,3,5-triazine (6) and 3,5-diphenyl-1,2,4-oxadiazole (7) are readily accounted for in terms of reactions of the primary products benzonitrile[6,13] and benzonitrile oxide.[4] Further, the rearrangement of benzonitrile oxide to phenyl isocyanate is well documented.[4,14] The formation of tribenzamide (8) is more difficult to rationalize.

The thermal fragmentation suggested in Scheme I is in very good agreement with the electron impact induced fragmentation of 5 as observed by mass spectrometry (Figure 3).

Correlation of mass spectral, thermal and photochemical reactions has received considerable attention in recent years.[15-25] The work of Dougherty[15,16] in expanding Dewar's PMO method[26] to predict and explain such correlations is of special importance. Dougherty has shown that it is often possible to deduce the level of electronic excitation of a

8

species which has undergone fragmentation in the mass spectrometer by critically examining its mass spectrum.[15] In particular, he states[15] that mass spectral reactions which occur from low-lying doublet or singlet states correlate with thermal reactions. He further states that such reactions include "all reactions of molecule ions which give rise to significant metastable peaks, and decomposition reactions of even electron ions that were initially formed in low-lying singlet states".[15]

In further work concerning the mass spectra of mesoionic compounds,[18] Dougherty obtained results which are particularly applicable to the present discussion. He found that calculation of π bond orders using simple ω-HMO theory,[27] allowed prediction of mass spectral ring cleavage reactions for methyl sydnone (10), phenyl sydnone (11), 4,5-diphenyl isosydnone (12), and a series of seven Ψ-1,3,4-thiadiazole-2-thiones (13). Furthermore, in the case of phenyl sydnone, for which pyrolysis data were available,[28] Dougherty[15] was able to explain the extent to which mass spectral and thermal cleavage were the same by application of π bond order arguments.

(10, R = Me; 11, R = Ph)

12

13

9
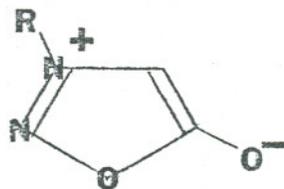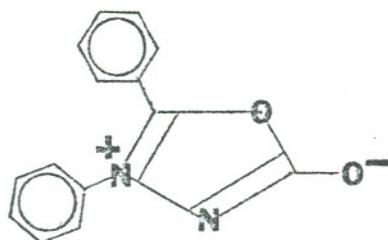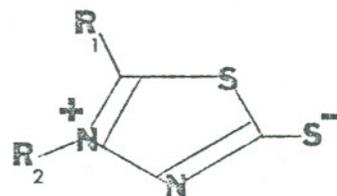
Dougherty makes clear[18] that for bond order arguments to be of value in predicting a mass spectral fragmentation, the fragmenting species must be in or very near its electronic ground state. The mesoionic compounds considered by him did fragment in an unexcited state as evidenced by the presence in the mass spectra of the compounds of metastable peaks corresponding to each predicted fragmentation.[18]

It follows then that if a given molecule fragments in accordance with its calculated ground state π bond orders, it is likely fragmenting in an electronically unexcited state, and should exhibit the same behavior upon pyrolysis.[18,23]

As Dougherty points out,[18] the calculation of π bond orders for a mesoionic molecule and the use of such bond orders to predict fragmentation is simply an extension of the usual resonance theory approach. He further states that with the exception of using π bond orders when considering mesoionic species, rather than the conventional valence bond diagrams, all the usual ground state organic chemical reasoning may be applied.[18] Thus, one decides which bond in a mesoionic compound is likely to be the most easily broken by examining calculated bond orders. Then one estimates the stability of the resulting products by the usual arguments from bond energy and intuition.[18]

A simple HMO calculation[27] was performed on the unsubstituted 3,4-diazacyclopentadienone-3,4-dioxide. The parameters used in the calculation,[27] the total π bond orders found, the atomic charge densities calculated for the highest occupied molecular orbital, and the π energy levels found are shown in Figure 1. Atomic orbital coefficients are listed in the appendix.

<center>π Bond Orders   HOMO Electron Densities</center>

$$\alpha_O = \alpha_O + \beta$$

$$\alpha_{\overset{+}{N}} = \alpha_O + 2\beta$$

$$\beta_{C-O} = \beta$$

$$\beta_{N-O} = 0.7\beta$$

$$\beta_{C-N} = \beta$$

$$\beta_{N-N} = \beta$$

Energy levels (from high to low):

$$\alpha - 1.5\beta$$
$$\alpha - 0.7\beta$$
$$\alpha$$
$$\alpha + 0.2\beta$$
$$\alpha + 0.7\beta$$
$$\alpha + 0.8\beta$$
$$\alpha + 1.96\beta$$
$$\alpha + 2.0\beta$$
$$\alpha + 3.55\beta$$

Energy ↑
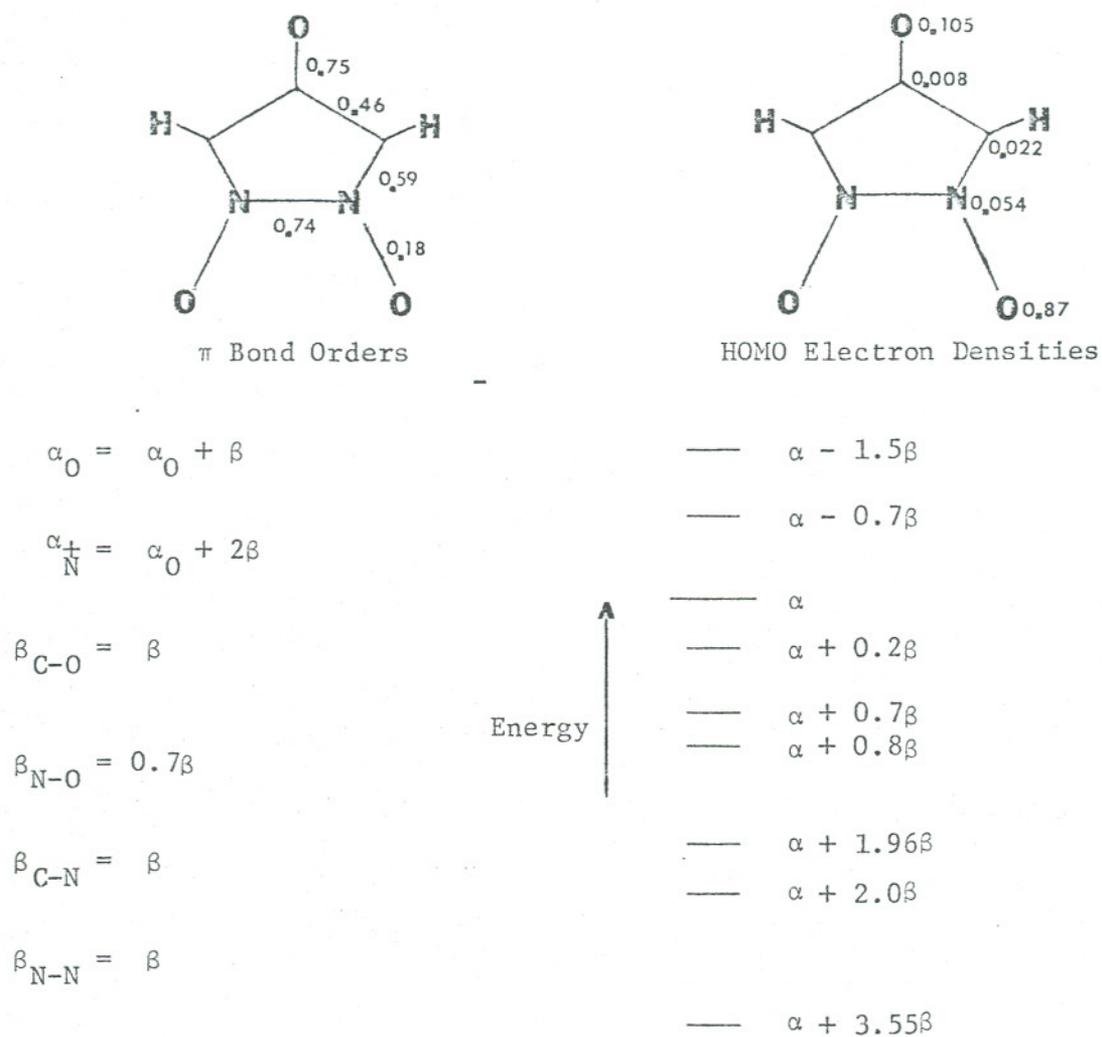
FIG. 1 HMO parameters, bond orders and HOMO electron densities of 3,4-diazacyclopentadienone-3,4-dioxide (2).

Since the prediction of a strong N–N π bond defies chemical intuition, atom bond and mutual bond polarizabilities, which are measures of the sensitivity of the N–N π bond order (P_{N-N}) to changes in the coulomb integral α_N and to changes in the resonance integrals β_{N-N}, β_{C-N} and β_{N-O} respectively, were calculated. The values which are listed below indicate no strong dependence of P_{N-N} on the indicated parameters, which means that our simple HMO calculation cannot be improved by choosing a different value for one of these parameters.

<center>11</center>

However, the calculation can be improved through application of the ω-technique[27] which takes account of some electron repulsion effects neglected in the present calculation.

$$\frac{\partial P_{N-N}}{\partial \alpha_N} = -0.027\beta^{-1} \qquad\qquad \frac{\partial P_{N-N}}{\partial \beta_{C-N}} = -0.077\beta^{-1}$$

$$\frac{\partial P_{N-N}}{\partial \beta_{N-N}} = 0.121\beta^{-1} \qquad\qquad \frac{\partial P_{N-N}}{\partial \beta_{N-O}} = -0.012\beta^{-1}$$

On the other hand, the 1,3 dipolar character of this heterocyclic system is well documented.[2] Thus, the N-N π bond order as well as the HOMO charge densities found here probably reflect a significant contribution from such resonance forms as 14 and 15 to the resonance hybrid of the system.

14   15
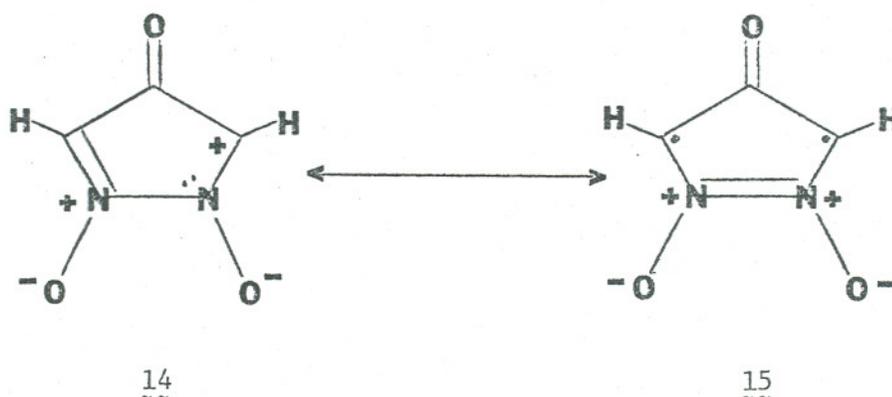
Assuming ground state electronics, the π bond orders calculated for the ring system indicate that initial fragmentation should take place at the bond α to the carbonyl group. There will of course be a new set of bond orders for the fragmented species, and these new bond orders will determine the second fragmentation.[18] However, one should also be able to determine the second fragmentation by consideration of the relative stabilities of products.[18] Thus, given fragment ion 16 below, one would predict fragmentation of the N-N bond to occur next to form 17 and HCNO.

12

16   17
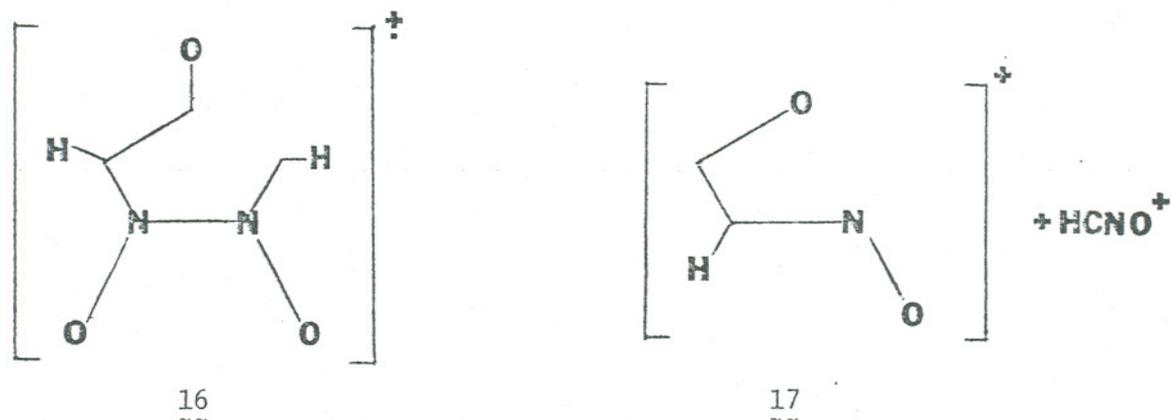
Thus for a 2,5 disubstituted derivative of the heterocycle (2), one

would expect ions P-RCNO and RCNO, and examination of the 70 ev mass

spectrum (Figure 2) of 2,5-dicarbomethoxy-3,4-diazacyclopentadienone (18)

reveals the expected pattern. The parent ion (m/e 230) is not observed

while the P-MeCO$_2$CNO ion (m/e 129) gives rise to the base peak in the

spectrum. The MeCO$_2$CNO ion (m/e 101) is also prominent.

18
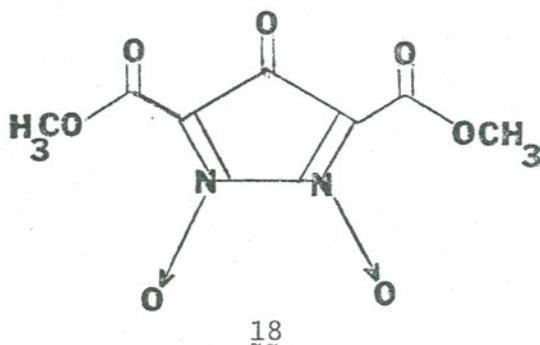
Examination of the 70 ev mass spectrum of the 2,5-diphenyl derivative

(5) reveals in addition to the expected P-PhCNO ion (m/e 147) a significant

P-NO ion (m/e 236) (see Figure 3). As shown in Scheme II, such a frag-

mentation seems best explained by initial cleavage of the N-N bond which

would produce a species (19) with considerable resonance stabilization

due to the presence of the phenyl groups. Note that 19 corresponds to

5A in Scheme I.

13
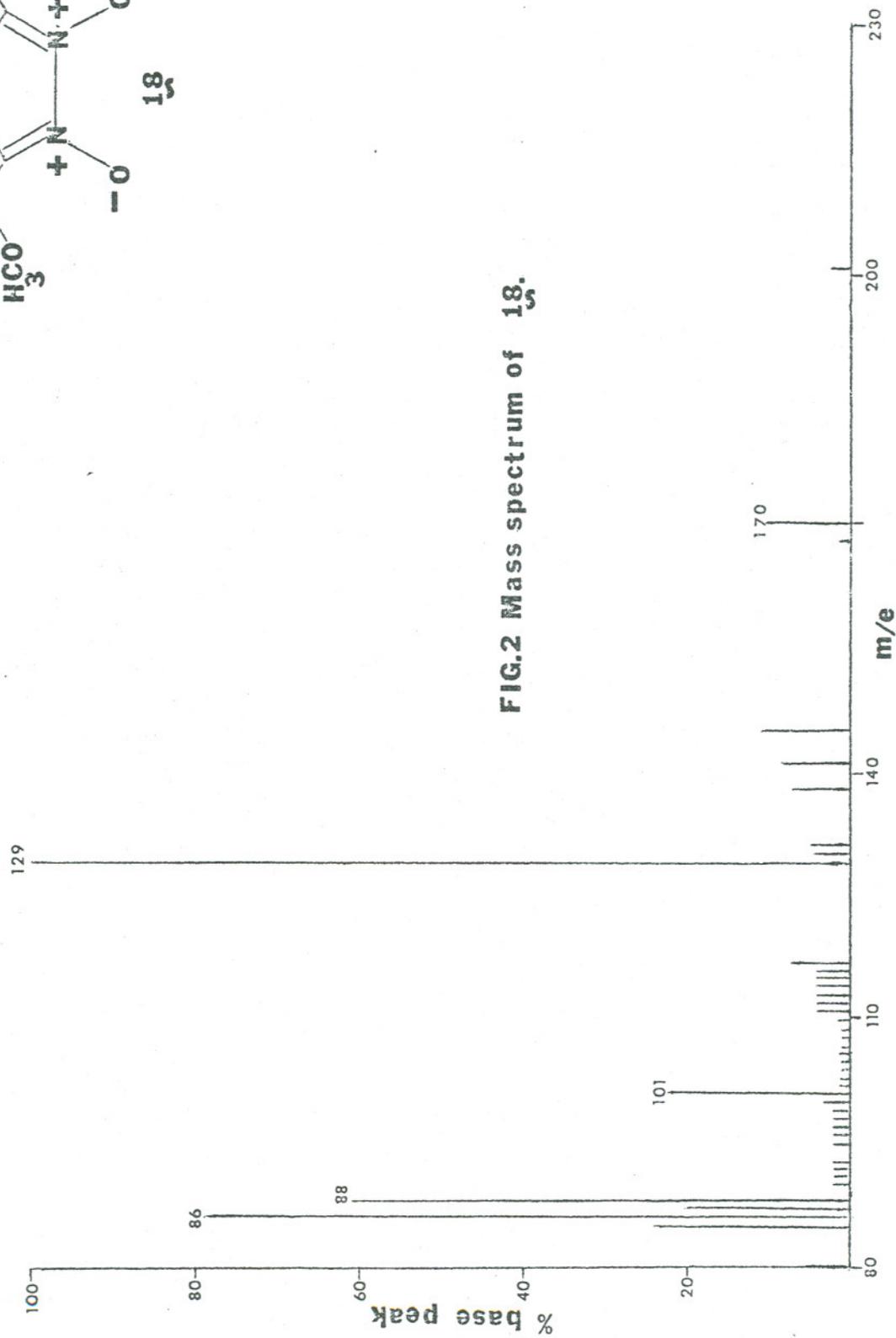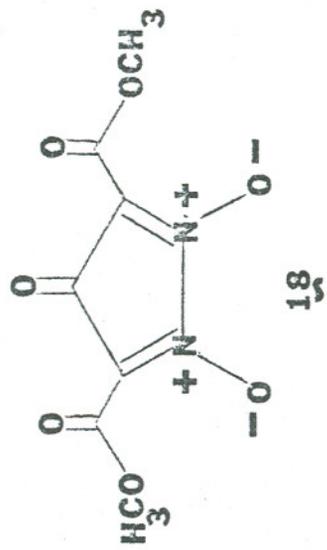
FIG.2 Mass spectrum of 18.

FIG.3 Mass spectrum of 5.

m/e 266

19

22

m/e 147

m/e 119

20

$\left[CO_2 \right]^{+\cdot}$ +

m/e 44

m/e 103

$\left[NO \right]^{+}$ +

m/e 30

m/e 236

21
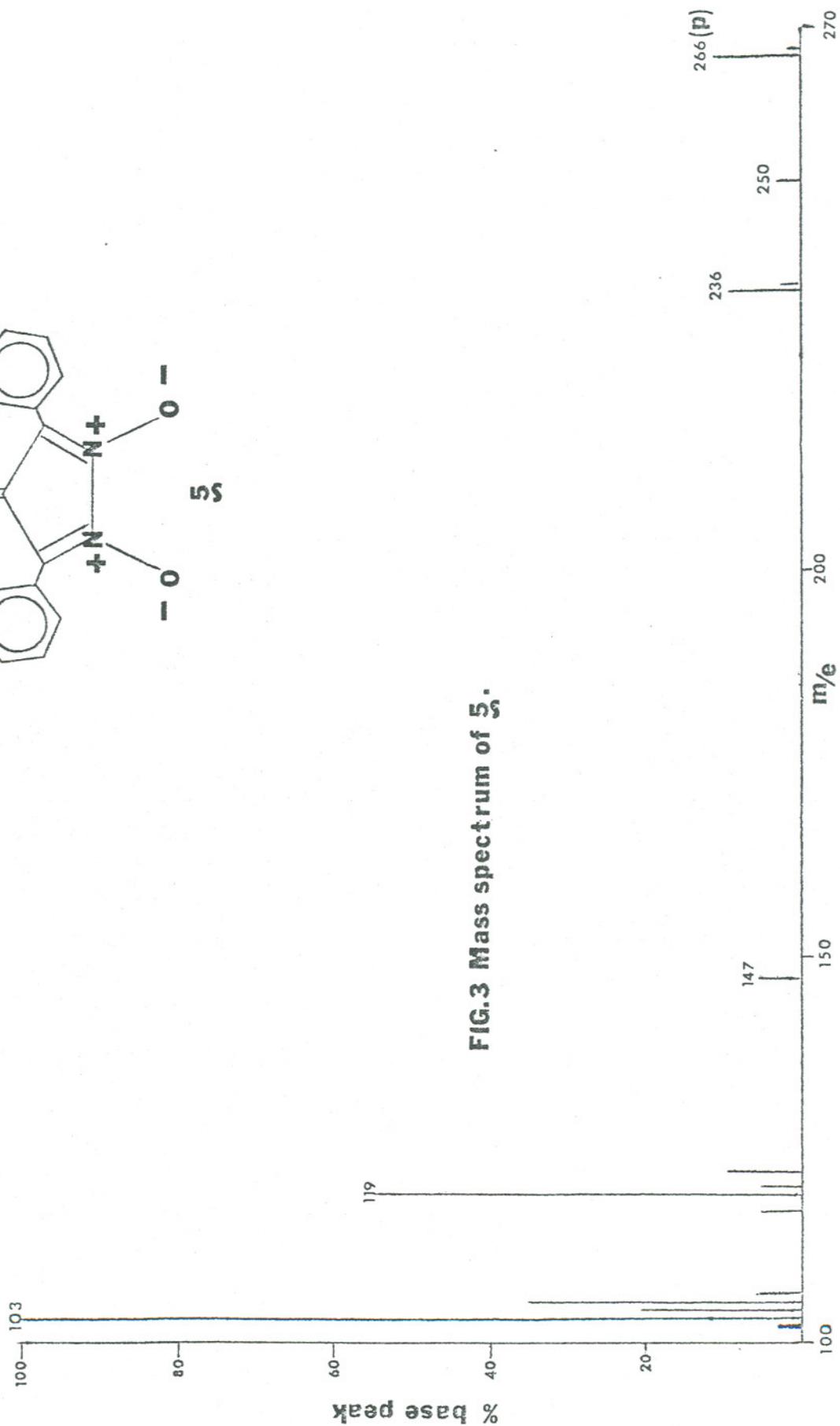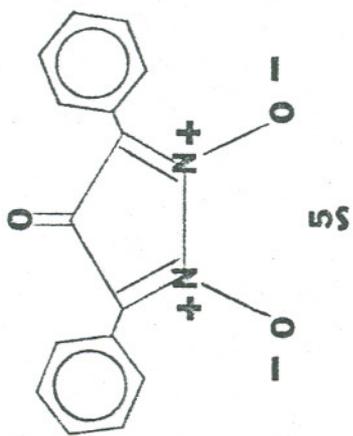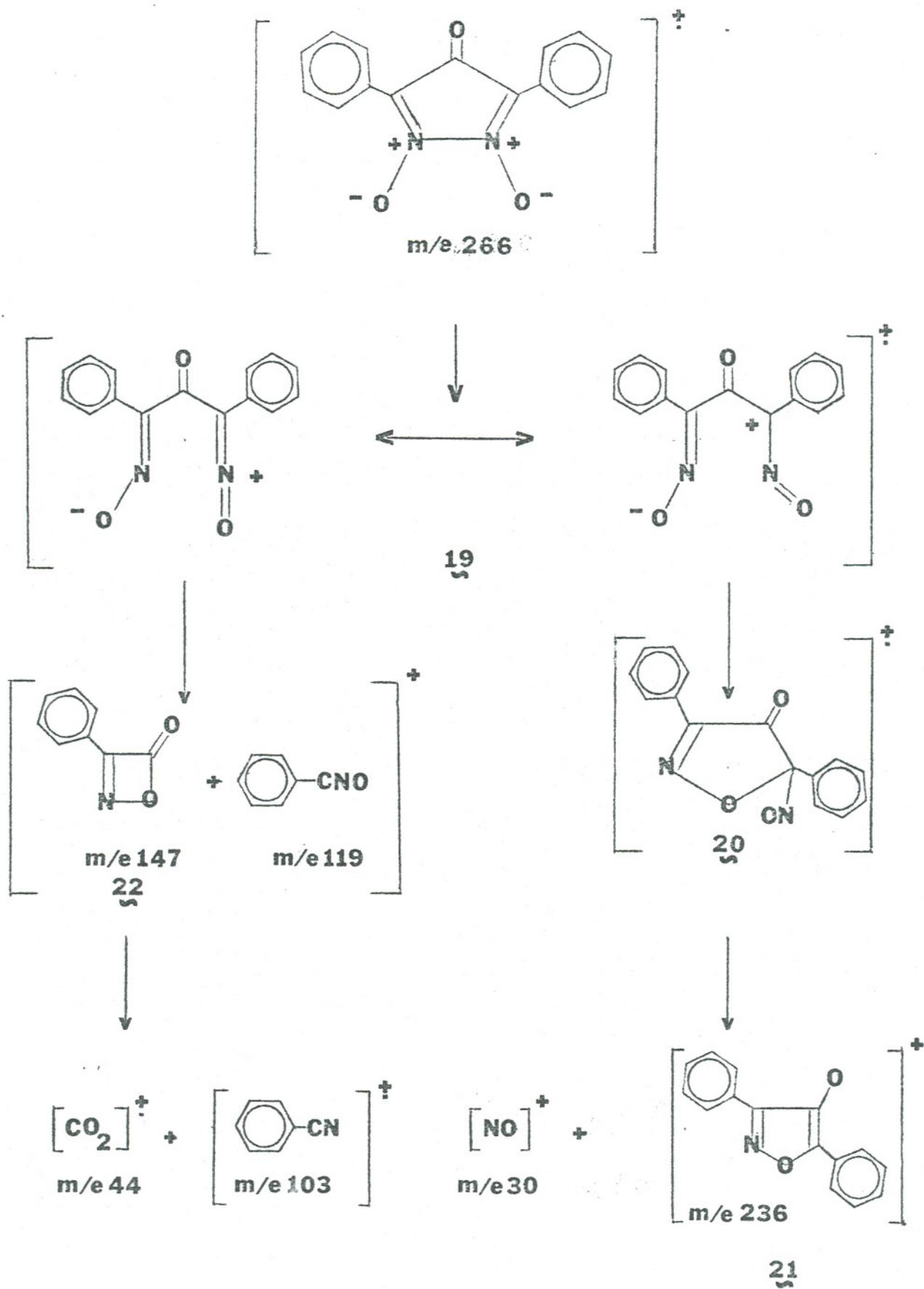
Scheme II electron impact fragmentation of 5.

As in Scheme I, cleavage of the C-C bond alpha to the carbonyl must compete with attack by oxygen at the positively charged α-carbon in 19. Attack at the α-carbon results in loss of NO to yield another highly resonance-stabilized ion (21).

Cleavage of the C-C bond alpha to the carbonyl in 19 would result in formation of the ion predicted from the earlier bond order arguments. This ion could then close to give 22 and expel carbon dioxide to yield benzonitrile which gives rise to the base peak in the spectrum. The fact that the diphenyl derivative (5) does not fragment exclusively according to the prediction of the bond orders calculated for the unsubstituted heterocycle is not surprising. It is likely that the initial N-N cleavage operates in addition to the predicted initial cleavage rather than with exclusion of the latter. Furthermore, it is likely that the presence of the phenyl groups alters the bond orders themselves sufficiently to account for the observed behavior.

The above rationalizations for the behavior of 5 are to be preferred over arguments that it reacts in an excited state in the mass spectrometer since the electron impact fragmentation can be reproduced by pyrolysis of the compound as described. In contrast, the ultraviolet irradiation of a methylene chloride-carbon tetrachloride solution of 5 through Pyrex for a period of 28 hr produced no significant reaction.

The earliest synthesis of what is now known to be the 2,5-dicarboethoxy derivative of 1 was reported by Henry and Pechmann in 1893.[29] They described the treatment of diethyl 1,3-acetonedicarboxylate with fuming nitric acid, and proposed structure 24 for the product as shown in equation 3. However, Freeman and coworkers[1] have found that

23   24
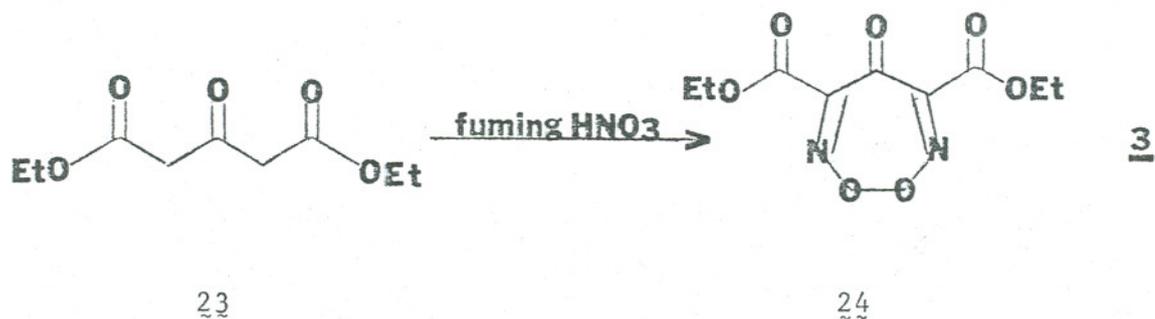
the most general method for synthesis of alkyl and aryl disubstituted derivatives of 1 is treatment of β-alkyl or aryl α,β-unsaturated oximes with nitrous acid under oxygen as exemplified by equation 4. They also
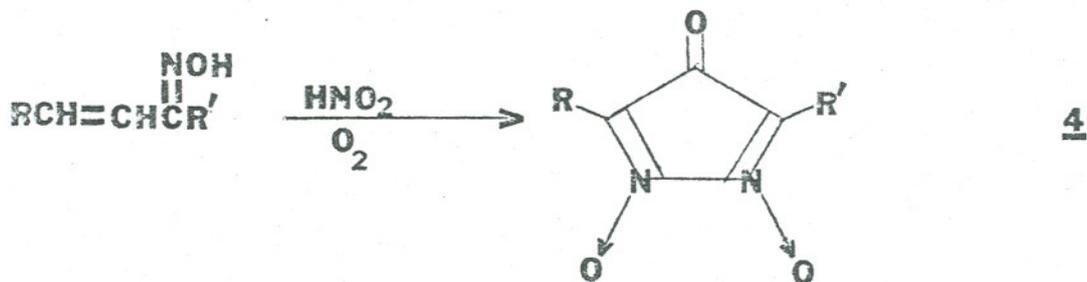
reported the oxidative ring closure of diphenyl triketone 1,3-dioxime (25)[30] upon treatment with sodium hypochlorite to yield the diphenyl derivative (5). This reaction is shown in equation 5. All three of the preceding transformations give low yields (20-30%) of the desired heterocycles.[1]

25   5
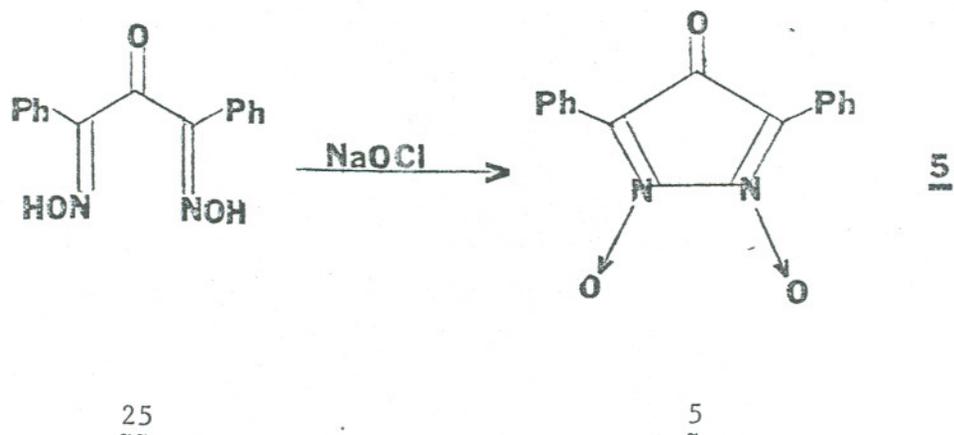
Shown in equation 6 is the simple synthetic sequence proposed for
the synthesis of 2. The first step in equation 6 is described by
Geismann et. al.[31] and is easily accomplished. Thus a cold aqueous
solution of 26 was treated with aqueous sodium nitrite. The product

26   27   2
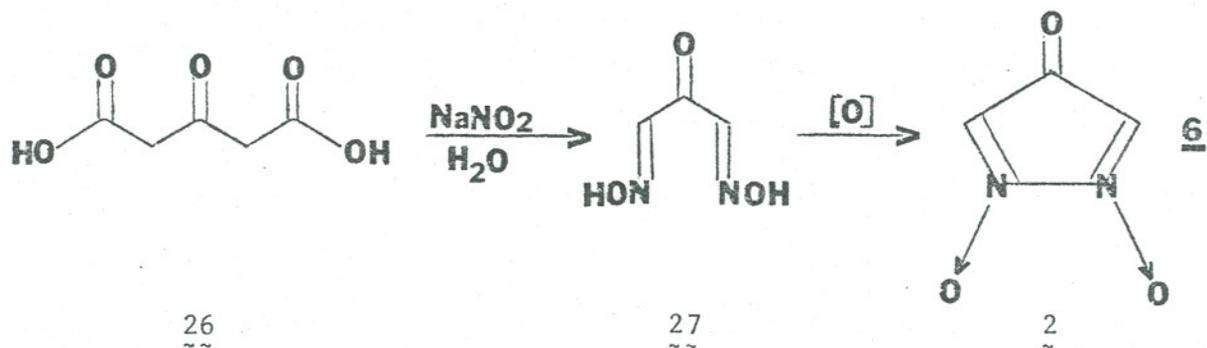
which precipitated was filtered and washed with ice water. When the

unsubstituted keto-dioxime (27) was treated with sodium hypochlorite

solution under conditions which caused ring closure in the 1,3-diphenyl

compound,[1] no reaction was observed as evidenced by thin layer

chromatography. In a slight variation, an attempt was made to promote

ring closure of 27 using boron trifluoride etherate as a catalyst as

shown in equation 7. Thus, a solution of 27 in ethyl acetate was treated

with a catalytic amount of boron trifluoride etherate. Only starting

material was present, as indicated by thin layer chromatography, after

one hour of heating the reaction mixture under reflux.

19
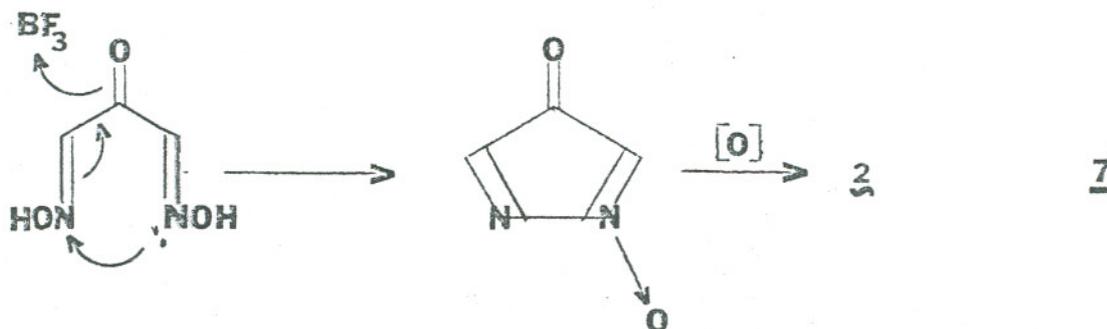
27

In 1905, Henle and Schupp[32] described the action of nitrogen trioxide
on an ethereal suspension of diisonitroso acetone (27). They reported
the formation of large red crystals which exploded on warming, became
straw-yellow in air, and were stable in concentrated sulfuric acid,
while water and dilute acids caused gas formation. Cold aqueous solutions
of alkaline salts reacted explosively with the crystals.

The properties of the red crystals isolated by Henle and Schupp
are consistent with those expected for the target molecule (2) since
a simple HMO calculation (Figure 1) predicts that 2 should have six
bonding molecular orbitals, two of which are empty. This suggests
that the molecule should behave as a powerful Lewis acid, and that the
molecule is highly susceptible to nucleophilic attack.

In attempts to reproduce the results reported by Henle and Schupp,
ethereal suspensions of 27 were treated with nitrogen trioxide (N_2O_3)[33]
in the cold (-74°), at room temperature, and with slow warming from
-74° to room temperature. In all attempts, the product isolated was a
colorless crystalline solid whose spectral properties and elemental
analysis were consistent with those of a polymer highly substituted
with carboxylic acid and alcohol functionalities.

20

EXPERIMENTAL

General Comments.

Melting points were determined on a Kofler microscope hot stage, and are uncorrected. Infrared spectra were obtained with a Perkin-Elmer model 337 grating spectrometer. Ultraviolet spectra were obtained with a Perkin-Elmer model 202 spectrometer. Nuclear magnetic resonance spectra were determined with a Varian model HA-100 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained with a CEC model 21-110B mass spectrometer using an ionizing voltage of 70 ev. The first number denotes m/e and the number in parentheses is the relative percent of the base peak. Microanalyses were done by Micro-Tech Laboratories, Skokie, Illinois. Photolysis was done with a PEK model 911 ultraviolet lamp. All solvents were reagent grade, and were used without further purification. Thin layer chromatography (TLC) was done on E. Merck silica gel G.

Preparation of 2,5-dicarbomethoxy-3,4-diazacyclopentadienone-3,4-dioxide (18).[1]

2,5-dicarbomethoxy-3,4-diazacyclopentadienone-3,4-dioxide (18) was prepared as described[1] to yield a yellow solid (20%); needles from methanol, mp 180-182°, sinters 169-170°, (lit,[1] mp 168-169°). $\lambda_{max}^{CH_3OH}$ 229, 283, 349-360 nm, (ϵ 15,200, 6,200), (lit,[1] ϵ 15,800, 6,870, 170); ν_{max}^{KBr} 2950, 1715, 1640, 780 cm^{-1}; nmr, (d$_6$ DMSO), δ 3.98(s); mass spectrum, (see Figure 2).

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<u>Preparation of 2,5-diphenyl-3,4-diazacyclopentadienone-3,4-dioxide</u> (5).[1]

2,5-diphenyl-3,4-diazacyclopentadienone-3,4-dioxide (5) was prepared
as described[1] to yield red crystals (26%); mp 190-195°, (lit,[1] mp 191-192°).
ν^{KBr}_{max} 3080, 1655 (shoulder), 1635, 1450, 780 (shoulder), 760 cm^{-1}; nmr,
(CDCl$_3$), δ7.50 (6H, m), 8.32 (4H, m); mass spectrum, (see Figure 3).

<u>Thermochemistry of 2,5-diphenyl-3,4-diazacyclopentadienone-3,4-dioxide</u> (5).

I. Fusion.

A. 2,5-diphenyl-3,4-diazacyclopentadienone-3,4-dioxide (5, 0.1 g)
    was placed in a Pyrex tube fitted with a Dewar cold finger cooled
    with Dry Ice in acetone. The tube was immersed in a silicone oil
    bath, and the bath temperature was raised to 195°, during 30 minutes,
    at which point the solid formed a red melt which degassed explo-
    sively. An infrared spectrum of the residue in the pyrolysis
    tube showed $\nu^{liq.\ film}_{max}$ 3060, 2230 (C≡N)[5], 1785, 1725, 1445, 758,
    688 cm^{-1}. Vapors produced were condensed on the cold finger to a
    light yellow liquid which was washed into a small flask with carbon
    tetrachloride. This solution and a carbon tetrachloride solution
    of the residue in the pyrolysis tube were examined by TLC (benzene).
    The chromatograms were similar and showed the presence of at
    least four compounds in addition to starting material.

B. Another 0.1 g sample of 5 was fused, and the fusion products from
    pyrolyses A and B were combined in benzene and separated by
    preparative thin layer chromatography (1 mm, silica gel PF$_{254}$
    developed 3 times with benzene). Sixteen bands were evident on
    the developed plates. Low resolution mass spectra were obtained
    of each of the sixteen separated compounds. Structures were

elucidated for two of the compounds, 2,4,6-triphenyl-1,3,5-triazine[6] (6) and 3,5-diphenyl-1,2,4-oxadiazole[8] (7), by mass spectrometry and comparison of melting points and ultraviolet spectra with those of authentic materials.[6,8,9]

Compound	Chromatography Band	Parent ion m/e	
	1 (origin)	122	
	2	286,	222
	3	286	
	4	286	
	5	345	
	6	222	
	7	357,	325
	8	357,	325
	9	182	
	10	297	
	11	210,	179
7	12	222	
	13	384	
	14	384,	385
	15	384,	309
6	16	309	

2,4,6-triphenyl-1,3,5-triazine (6).[6]

Band 16 yielded 1 mg of a colorless solid, mp 180-200°. Further chromatography of this material (silica, 1 mm, developed with 10:1 cyclohexane:ether) gave 0.5 mg of colorless crystals, mp 190-210°, (lit,[6] mp 235°). λ_{max}^{hexane} 270 nm; authentic 6 prepared by the method of Cook and Jones,[6] exhibited λ_{max}^{hexane} 270 nm (ε 67,500); a low resolution mass spectrum of the isolated material had prominent peaks at 309 (22) P, 205 (4.4), 103 (100). Exact masses were determined by high resolution mass spectrometry.

m/e	Composition	Calculated Mass	Found m/e
309	$C_{21}H_{15}N_3$	309.1265	309.1277
205	$C_{14}H_9N_2$	205.0766	205.0770
103	C_7H_5N	103.0422	103.0427

<u>3,5-diphenyl-1,2,4-oxadiazole</u> (7).[8,9]

Band 12 yielded 7 as colorless needles (1 mg), mp 68-103°, (lit,[7] mp 108°); λ_{max}^{ETOH} 248 nm, (lit[9] λ_{max}^{Ether} 245 nm, (ϵ 37,200)); mass spectrum, 223 (19), 222 (100) P, 119 (86), 105 (20), 103 (20).

II. Solution pyrolyses of 2,5-diphenyl-3,4-diazacyclopentadienone-3,4-dioxide (5).

A. Compound 5 (0.3 g) was dissolved in 30 ml of nitrobenzene, and the solution was heated under reflux for 1 hr. Brown fumes (NO_2) were present above the solution throughout the period of heating. After vacuum distillation of the nitrobenzene, a brown tarry residue remained which was shown by TLC (carbon tetrachloride) to be a complex mixture. No products were characterized.

B. Compound 5 (0.3 g) in 30 ml of benzene was heated under reflux for 8 hr. At the end of this time, TLC (developed with carbon tetrachloride, benzene, 1:1 benzene:acetone) showed only starting material to be present.

C. Compound 5 (0.3 g) in 30 ml of toluene, was heated under reflux for 72 hr at the end of which time TLC (benzene) showed the presence of small amounts of two compounds in addition to starting material.

D. Compound 5 (0.3 g) in 30 ml of bromobenzene was heated under reflux for 5 hr during which time brown fumes were visible over the reaction mixture. Bromobenzene was removed from the mixture under reduced pressure leaving a viscous, oily residue whose infrared spectrum (liquid film) was essentially the same as that of the fusion residue (see Fusion A) except that the band at 2230 cm^{-1} was not present.

E. Experiment D was repeated using a nitrogen atmosphere and a nitrogen purged solution of 5. At no time were brown fumes observed above the reaction mixture.

Quantitative detection of carbon dioxide.

2,5-diphenyl-3,4-diazacyclopentadienone (5, 2.00 g, 0.008 mole) was dissolved in 200 ml of bromobenzene in a 3-necked flask fitted with a reflux condenser and a nitrogen inlet. The mixture was heated at reflux for 5 hr while nitrogen was swept into the flask to carry product gases out through the reflux condenser and into a gas train consisting of two tared 50 ml centrifuge tubes and a 500 ml Erlenmeyer flask connected in series. The tubes and flask each contained a saturated solution of barium hydroxide. As the pyrolysis proceeded, barium carbonate precipitated in the two tubes while no barium carbonate precipitated in the large flask which was the last trap in the series. Note that two blanks were run which consisted of saturated barium hydroxide solutions through which nitrogen and carbon monoxide were passed for one hour and three minutes respectively. No precipitate was observed in either blank.

The tubes containing the precipitate were centrifuged, and the supernatant solution was decanted from them. The precipitate was washed

with 3x30 ml portions of distilled water, and dried to constant weight at 150°. The total weight of dry barium carbonate was 0.83 g (0.004 mole).

Bromobenzene was removed from the reaction mixture under reduced pressure to leave a red viscous oil. The oil was dissolved in a small amount of benzene and the solution was chromatographed on a column (Mallinckrodt Silica AR CC-7, 100-200 mesh, eluted with benzene). The materials isolated are listed below in the order in which they were eluted from the column.

Fraction	Compound	Melting Point	Amount
1	2,4,6-triphenyl-1,3,5-triazine	234-237° (lit[6] 235°)	2 mg (0.1%)
2	Starting material	190-195° (lit[1] 191-192°)	30 mg (1.5%)
3	plates	200-206°	4 mg (0.2%)
4	tribenzamide	205-212° (lit[10] 211-212°)	10 mg (0.5%)

Fraction 1 yielded 2,4,6-triphenyl-1,3,5-triazine (6, 2 mg) identified by comparison of the melting point and ultraviolet spectrum with those of authentic material.[6]

Fraction 2 produced starting material (5, 2 mg) identified by its melting point.[1]

Fraction 3 yielded plates (4 mg), mp 200-206°. $\lambda_{max}^{CH_3OH}$ 240 nm, 280 nm; ν_{max}^{KBr} 1744, 1717, 1340, 1285, 1242, 905, 712, 692 cm^{-1}; the mass spectrum had prominent peaks at 445 (3.3), 444 (9.3) P, 340 (2.7), 105 (100). The structure of this compound was not elucidated.

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Fraction 4 produced tribenzamide ($\underline{8}$, 10 mg, mp 200-205°) identified by comparison of the melting point and infrared spectrum with those of authentic material.[10] $\lambda_{max}^{CH_3OH}$ 250 nm, (ϵ 32,800); ν_{max}^{KBr} 1695, 1236 cm^{-1}; nmr, ($CDCl_3$), δ7.48 (9H, m), 7.86 (3H, d, J = 8Hz), 7.88 (3H, d, J = 8Hz); the mass spectrum had ions at 329 (21) P, 301 (19), 227 (16), 226 (100), 225 (15), 224 (32), 198 (19), 122 (11), 121 (10), 106 (65), 105 (off scale), 103 (52.5).

The organic material remaining on the column after elution of tribenzamide was a mixture of at least 30 compounds (1.17 g) which could not be adequately separated and were not identified.

Quantitative detection of benzonitrile.

2,5-diphenyl-3,4-diazacyclopentadienone-3,4-dioxide ($\underline{5}$, 2.00 g) in 200 ml of diglyme was heated under reflux for 3 hr after which time the solution was a pale yellow. The diglyme was distilled under reduced pressure with steam heating during 2 hr, and small portions of fresh diglyme were occasionally added to the pot to facilitate distillation of all volatiles. A 0.5 ml sample of the distillate was pipetted into a 5 ml volumetric flask, and diluted to 5 ml with diglyme after which 0.5 ml of the resulting solution was taken and diluted to 5 ml with diglyme. The secondary band of benzonitrile, $\lambda_{max}^{H_2O}$ 271 nm, (ϵ 1000)[5], was used to calculate the concentration of benzonitrile in the solution. The distillate contained 0.004 mole of benzonitrile.

Mass spectral gas analysis.

Compound $\underline{5}$ (0.2 g) was placed in a glass tube which was sealed at one end and fitted with a male 10/30 ground glass joint. The tube was

evacuated ($P = 10^{-6}$ micron) and a break off seal was fashioned inside the tube. The tube was heated in a bomb oven at 160° for 24 hr then at 180° for an additional 24 hr. After cooling, it was connected to the gas inlet system of the mass spectrometer.

An initial low resolution spectrum of the mass spectrometer background (excluding gas train) showed no peaks on the 1x scale of the strip chart recorder.

A low resolution scan of the gas mixture showed the following:

m/e	% Base Peak
28	39
30	20
44	100

High resolution strip chart recording revealed the peaks at nominal masses 28 and 44 to be doublets. The peak at m/e 30 was a singlet. The two peaks at m/e 28 were assumed to be nitrogen and carbon monoxide. Nitrogen was confirmed by admitting a mixture of air and sample gases into the spectrometer. The peaks at m/e 44 were assumed to be carbon dioxide and nitrous oxide. Nitrous oxide was confirmed by admitting a mixture of nitrous oxide and sample gases into the spectrometer. Using the exact mass of carbon monoxide, the masses of the other m/e 28 peak (nitrogen) and of the m/e 30 peak (nitrogen monoxide) were measured by peak matching, and by assuming the exact mass for carbon dioxide, the exact mass of the other m/e 44 peak (nitrous oxide) was calculated.

Gases peak matched to CO, m/e = 27.994914

Gas	Calculated Mass	Found m/e
N_2	28.00614	28.00634
NO	29.99798	29.99761

Gases peak matched to CO_2, m/e = 43.989828

| Gas	Calculated Mass	Found m/e
N_2O	44.00105	44.00109

High resolution strip chart recording at m/e 28, 30 and 44 allowed an estimate of the relative amounts of the five gases. Peaks from high resolution scans made at each mass within a 3 minute period were cut from the chart paper, weighed and the mole percentage of each gas was calculated to give the data shown in Table I. The precision was ± 1 to ± 5 mole% based on the method of analysis. The value for CO was corrected for CO_2 fragmentation.

Since a certain amount of air is always present in a mass spectrometer, it is important to demonstrate that air was not a significant contributor to the nitrogen peak observed. The mass spectrometer used in this experiment is known to record a ratio of approximately 4:1 for nitrogen to oxygen in air. The initial low resolution scan of the gas mixture showed a ratio of 37 mm:0.5 mm for the m/e 28:m/e 32 peak heights. Since the ratio of carbon monoxide to nitrogen was 1.1, nitrogen accounted for a peak height of 18 mm. Yet if one assumes the peak at m/e 32 is due to oxygen from air, a nitrogen peak height of 2 mm is predicted. Clearly, the observed nitrogen to oxygen peak height ratio rules out the presence of a significant amount of air in the instrument.

The glass tube in which the pyrolysis was done contained a small quantity of yellow oil the infrared spectrum of which showed it to be a mixture of benzonitrile and phenyl isocyanate.

Determination of the mole percentage of benzonitrile and phenyl isocyanate in the pyrolysate derived from the above experiment.

Mixtures of benzonitrile and phenyl isocyanate were examined by infrared spectroscopy in the 2230-2268 cm^{-1} region. Benzonitrile and phenyl isocyanate were weighed out into a series of tared vials in the ratios: (given as PhCN g/PhNCO g) 9.8/1, 5.3/1, 4.25/1, 3.06/1, 2.04/1, 1/1, 1/5, 1/10. These weight ratios were plotted versus the PhCN/PhNCO peak height ratios. The peak heights were measured as shown below. With
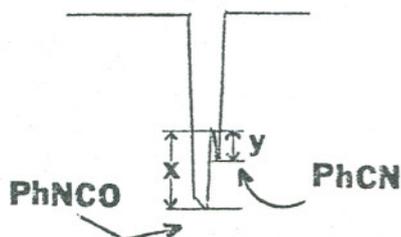
reference to the plot, the oil was found to have a composition of 2.4/1 PhCN/PhNCO by weight (74 mole% PhCN and 26 mole% PhNCO).

Kinetics of the disappearance of 2,5-diphenyl-3,4-diazacyclopentadienone-3,4-dioxide in refluxing bromobenzene.

Compound 5 (1.02 g, 0.0038 mole was dissolved in 50 ml of bromobenzene to give an approximately 7.6x10^{-2} M solution which was poured into a 250 ml round bottom 3-necked flask fitted with a reflux condenser and a thermometer for measuring the pot temperature. The solution was heated to reflux (pot temp. 157°), a 1 ml aliquot of the reaction mixture was withdrawn and an electric timer was started. Further 1 ml aliquots were withdrawn as

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indicated in the table below. The absorbance of the reaction mixture, $\lambda_{max}^{bromobenzene}$ 466 nm, was used to measure the rate of disappearance of starting material. The data were plotted on semi-log paper to yield an excellent straight line as shown in Figure 4. The rate constant and the half life of the reaction (157-158°) are k = 2.08×10^{-4} sec^{-1}, $t_{1/2}$ = 55.4 min. The free energy of activation at 157-158° is $\Delta G^{\ddagger}$ = 32.7 k-cal/mole.

Time (min ±3 sec)	Absorbance (466 nm)
0	1.21
10	1.05
20	0.92
30	0.82
40	0.74
50	0.64
60	0.57
75	0.46
90	0.37
120	0.27
180	0.15
240	0.09
300	0.07

Photolysis of 2,5-diphenyl-3,4-diazacyclopentadienone-3,4-dioxide (5).

The compound (5, 0.3 g) was dissolved in 60 ml of 1:1 methylene chloride:carbon tetrachloride and irradiated in a Pyrex flask for 28 hr after which time, TLC (benzene) showed the presence of slight amounts of two materials in addition to starting material.

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FIG.4 kinetics of disappearance of 5.

$$k = 2.08 \times 10^{-4} sec^{-1} \ (157\text{--}58^0)$$

$$t_{1/2} = 55.4 \text{ min.}$$
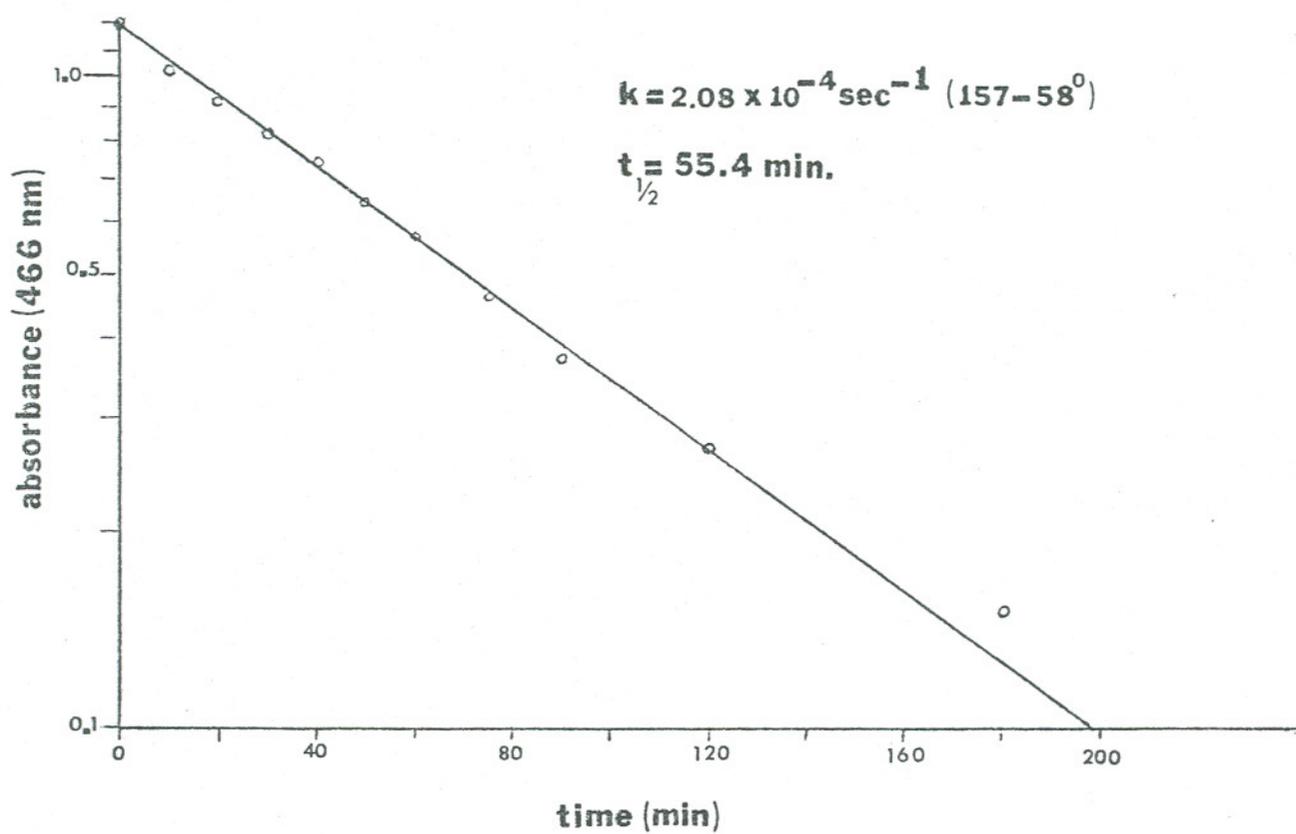
Preparation of 1,3-diisonitrosoacetone (2̰7̰).[31]

1,3-diisonitrosoacetone (2̰7̰) was prepared as described[30] to yield
a white powder (13 g, 77%). A small sample was recrystallized from
5:1 benzene:acetone, dec. 135° (lit[31] 133°). $\lambda_{max}^{CH_3OH}$ 255 nm (ε 12,000);
ν_{max}^{KBr} 3268, 1658, 1575, 1445 cm^{-1}; nmr, (DMSO d_6), δ7.95 (s).

Reaction of diisonitrosoacetone (2̰7̰) with sodium hypochlorite.

To a solution of 0.7 g of the keto-dioxime (2̰7̰) in 50 ml of 5%
aqueous sodium hydroxide was slowly added with stirring at room temperature,
10 ml of 5% sodium hypochlorite solution. No change in the reaction
mixture was observable. After the reaction mixture was stirred for 3 hr,
TLC (1:1 acetone:benzene) showed only starting material to be present.

Treatment of 1,3-diisonitrosoacetone (2̰7̰) with boron trifluoride etherate.

To 1,3-diisonitrosoacetone (2̰7̰, 0.1 g) in 20 ml of ethyl acetate was
added ten drops of 98% boron trifluoride etherate and the resulting solution
was heated under reflux for 70 min. At the end of this time, TLC (1:1
acetone:benzene) and an ultraviolet spectrum showed only starting material
to be present.

Reaction of 1,3-diisonitrosoacetone (2̰7̰) with nitrogen trioxide.[32,33]

A. Arsenic trioxide (20 g) was placed in a 100 ml 3-necked flask
fitted with a dropping funnel charged with 16 ml of nitric acid (d. 1.3).
The flask was attached to a gas train consisting of a 100 ml trap and a
drying tube containing calcium chloride. The nitric acid was added drop-
wise to the powdered arsenic trioxide, and the system was swept with

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nitrogen into a 50 ml tube supported in a Dry Ice acetone bath. After about 0.1 ml of blue liquid nitrogen trioxide[33] condensed in the tube, a slurry of 27 (0.1 g) in 9 ml of ether was added to it. A yellow solution resulted and about one half of the diisonitrosoacetone dissolved. The tube was removed from the cold bath, and gas was passed into the reaction mixture until all of the diisonitrosoacetone dissolved. The solution stood at room temperature for one week during which time the ether evaporated depositing clusters of colorless needles, mp 60° dec. $\lambda_{max}^{CH_3OH}$ 225-300 nm; ν_{max}^{KBr} 3400 (broad), 1685 (broad), 1260 cm^{-1}; nmr, (DMSO d$_6$) δ5.9 (broad), δ6.5-8.0 (broad), all signals disappear in D_2O. Anal. Calcd for $C_6H_{13}NO_{15}$: C, 21.25; H, 3.84; N, 4.14; O, 71.00. Found: C, 21.10; H, 3.73; N, 4.06; O, 71.11.

B. Nitrogen trioxide was passed into a slurry of diisonitrosoacetone (27, 0.1 g) in 3 ml of ether cooled in a Dry Ice acetone bath until a deep blue-green color persisted. The resulting mixture stood overnight in the bath during which time it warmed to room temperature, and became yellow. The solution stood at room temperature for one day during which time the ether evaporated depositing long colorless needles, mp 60° dec. $\lambda_{max}^{CH_3OH}$ 225-300 nm; ν_{max}^{KBr} 3400 (broad), 1685 (broad), 1260 cm^{-1}; Anal. Calcd for $C_{13}H_{19}NO_{29}$: C, 23.90; H, 2.92; N, 2.15; O, 71.10. Found: C, 23.98; H, 2.92; N, 2.18; O, 71.56.

C. Nitrogen trioxide was passed into a slurry of diisonitrosoacetone (27, 0.1 g) in 3 ml of ether at room temperature until the solids dissolved forming a clear yellow solution. The solution stood at room temperature for one day during which time the ether evaporated depositing colorless needles, mp 60° dec. ν_{max}^{KBr} 3400 (broad), 1685 (broad), 1260 cm^{-1}.

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APPENDIX

THE HÜCKEL MOLECULAR ORBITALS OF 3,4-DIAZACYCLOPENTADIENONE-3,4-DIOXIDE (2).
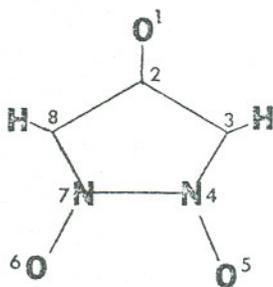
MO	ATOMS							
	1	2	3	4	5	6	7	8
1	0.054	0.168	0.227	0.634	0.174	0.174	0.634	0.227
2	0	0	0.601	0.303	0.212	-0.212	-0.303	-0.601
3	-0.490	-0.714	-0.276	0.180	0.130	0.130	0.180	-0.276
4	-0.230	-0.064	0.105	0.164	-0.658	-0.658	0.164	0.105
5	0	0	0.350	-0.242	0.565	-0.565	0.242	-0.350
6	0.779	-0.231	-0.353	0.162	-0.141	-0.141	0.162	-0.353
7	0	0	0.574	-0.383	0.157	-0.157	0.383	-0.574
8	0.313	-0.635	0.486	-0.112	0.031	0.031	-0.112	0.486

BIOGRAPHICAL NOTE

The author was born October 16, 1948 in Albuquerque, New Mexico. He attended Albuquerque public schools for twelve years and graduated from Rio Grande High School in May 1966, immediately after which he enrolled at New Mexico Institute of Mining and Technology. While enrolled in college, he worked part time for three years as a machinist's apprentice and for one year as an undergraduate chemical research assistant. He received his B.S. degree in chemistry from New Mexico Institute of Mining and Technology in June 1970.

In July 1970, he began graduate study at the Oregon Graduate Center where he completed requirements for the M.S. degree in chemistry in August 1972. He is leaving the Oregon Graduate Center to accept a graduate teaching assistantship at Stanford University in September 1972.