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Synthesis and Properties of Nitrocarbenes and Diazirinone

August 1990

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FOREWORD

This final report was submitted by the Chemistry Department of the University of Utah, Salt Lake City UT on completion of contract F04611-87-K-0023 with the Astronautics Laboratory (AFSC), Edwards AFB CA. AL Project Manager was Lt Roeland A. van Opijnen.

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The area of high energy density materials continues to receive a great deal of attention. This is due to the need to package more energy into a smaller volume. Highly symmetric compounds have high densities and the strain energy of highly strained compounds serves to increase their heat of formation and therefore lead to improved performance as propellants, explosives and fuels. This is not a new idea. Indeed, there is presently a large effort directed towards the preparation of energetic cubane derivatives. However, the synthesis of cubane derivatives has been a tremendous synthetic challenge and major breakthroughs in their preparation have been slow in coming. On the other hand, we have chosen to study less involved but still highly strained structures, namely cyclopropyl compounds. One class of such energetic compounds, the nitrocyclopropanes, has received minimal work. Over the past three years, we have developed efficient methodology for the formation and reactions of such systems based on nitrocarbene chemistry. This progress report details the preparation and reactions of some of these nitro compounds. A second area of research covered during the

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Block 19. concluded

grant period was a computational study of a novel, high energy density compound, diazirinone. In addition, our experimental attempts to prepare this compound are also included.

Block 18. concluded

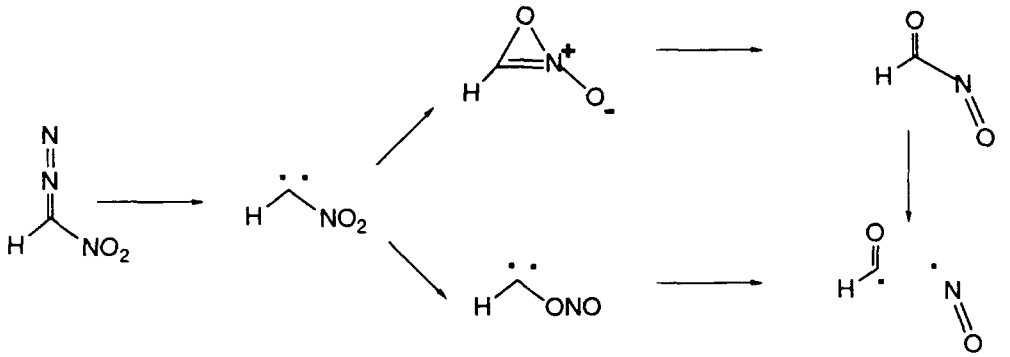
diazirines, diazo compounds

TABLE OF CONTENTS

SYNTHESIS AND PROPERTIES OF NITROCARBENES

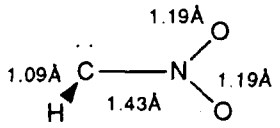
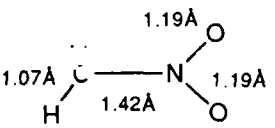
INTRODUCTION

Before we started our work in this area, there was relatively little known about the chemistry or structure of nitrocarbenes.[1] An ideal precursor to nitrocarbene, nitrodiazomethane, was prepared by Schollkopf and Markusch,[2] but they found that it failed to add nitrocarbene to alkenes under either thermal or photochemical conditions. Instead they found evidence that nitrocarbene fragments to formyl radical and nitric oxide. Possible pathways for this reaction are shown below.



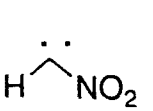
AB INITIO CALCULATIONS

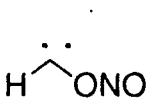
As a first step in the understanding of such species, we probed the potential energy surface for this system using ab initio molecular orbital theory.[3] One of the first questions we asked was "what is the ground state of nitrocarbene?" We have calculated the geometry optimized singlet and triplet states of nitrocarbene using the 6-31G* basis set and a two configurational wavefunction for the singlet state and a restricted open shell HF wavefunction for the triplet.[4] The results are shown below and lead to the conclusion that the two states are very close in energy.[5] This is different from other carbenes substituted by a conjugating electron withdrawing group which prefer triplet ground states.[6]

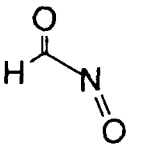
SINGLET	TRIPLET
	
H-C-N = 102.79^0	H-C-N = 121.85^0
TCSCF -242.37466	ROHF -242.37979 hartrees
REL. E 3.2 Kcal/mol	0.0

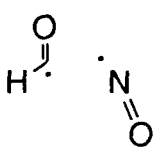
As a further guide in the understanding of this system, we calculated several local minima on the potential energy surface at the optimized HF/6-31G* level. Single point energy calculations partially corrected for electron correlation were performed using third order Møller-Plesset perturbation theory (MP3) and the 6-31G* basis set. The total and relative energies are shown

below for singlet nitrocarbene, singlet nitritocarbene, nitrosoformaldehyde, and free nitric oxide and formyl radical.



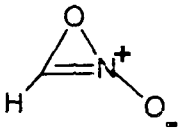




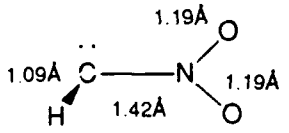


-E	242.98024	243.03113	243.14164	242.98523 hartrees
rel. E	101.3	69.3	0.0	98.1 kcal/mol

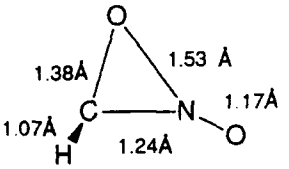
It is not surprising that the global minimum is nitrosoformaldehyde, while nitrocarbene is predicted to lie 101 kcal/mol higher in energy. We were unable to find a local minimum corresponding to oxazirine-N-oxide but we did locate a transition structure (see below) in this area of the potential energy surface.



The calculations reveal that the rearrangement of singlet nitrocarbene is highly favored on thermodynamic grounds. However, there may still be a substantial barrier to the rearrangement. Further calculations using the 6-31G* basis set and complete geometry optimization were performed on singlet nitrocarbene and the transition structure for oxygen migration. The nature of these stationary points (minimum and transition structure) was confirmed by analytical frequency calculations. These were followed by single point energy calculations using the 6-31G* basis set at the MP3 level in addition to multi-configurational SCF (MCSCF) calculations using three configurations. Partial geometries and the HF, MP3, and MCHF total energies for the singlet ground state of nitrocarbene and the transition structure for oxygen migration are shown below.



minimum



transition structure

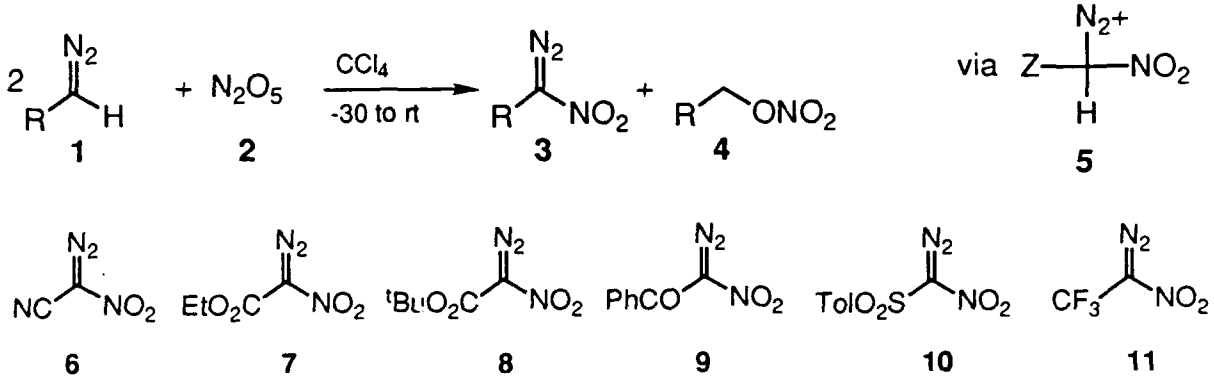
- E (HF)	242.35404	242.33370 hartrees
(MP3)	242.98024	242.99360 hartrees
(MCHF)	242.37453	242.37396 hartrees

If one takes zero-point energies into account, then the barrier to rearrangement at the HF/6-31G* level is calculated to be 12.4 kcal/mol while at the MP3/6-31G* level, the barrier is calculated to be much less than zero (-16.8 kcal/mol). The MP3 method, a non-variational procedure, appears to greatly overestimate the stability of the transition structure relative to the ground state. On the other hand, the MCSCF method, a variational procedure, predicts that the barrier is very close to zero. Further calculations at the HF/3-21G level reveal that this transition structure leads to nitrosoformaldehyde. Thus nitrocarbene is calculated to spontaneously rearrange to nitrosoformaldehyde. These results agree with the previous experimental observation[2] that nitrocarbene is a very labile species.

SYNTHESIS OF NITRODIAZOMETHANES

Nitrodiazo compounds are ideal precursors to nitrocarbenes and are potentially accessible via the introduction of a diazo group into a nitro compound or via the introduction of a nitro group into a diazo compound. Diazo group transfer with sulfonyl azides has made a range of diazo compounds accessible.[7] This reaction, unfortunately, is not applicable to nitro compounds.[8] An azidinium salt will transfer a diazo group to methyl nitroacetate and nitroacetophenone.[9] Attempts to extend this method to nitromethane or other nitro compounds were unsuccessful.[9b]

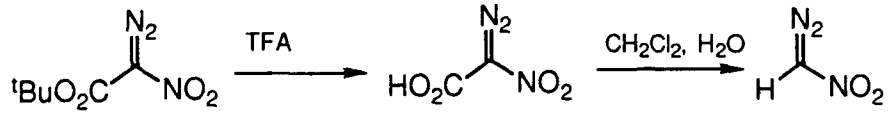
In the course of their studies on substituted carbenes during the 1960's, the Schöllkopf group developed a nitration procedure for electronegatively substituted diazo compounds.[10] Here, a solution of dinitrogen pentoxide (**2**) in halogenated solvent is added dropwise to the diazo compound **1** at low temperature. The reaction requires 2 equivalents of diazo compound, for the second mole acts as a base to deprotonate the intermediate diazonium ion **5**. Compounds **6-11** have been prepared by this method.



1 **2** **3** **4** **5**

6 **7** **8** **9** **10** **11**

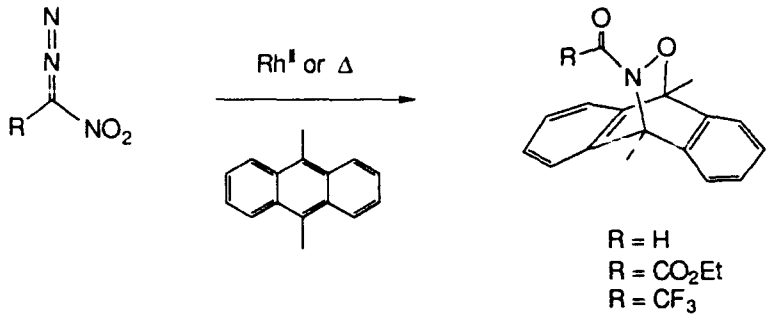
The application of this procedure to diazomethane or phenyl diazomethane failed. Presumably the intermediate diazonium ion **5** loses nitrogen before deprotonation occurs. The parent nitrodiazomethane (**13**) is prepared by deprotection of the t-butyl ester (**8**) with trifluoroacetic acid and proceeds via nitrodiazoacetic acid (**12**).[11]



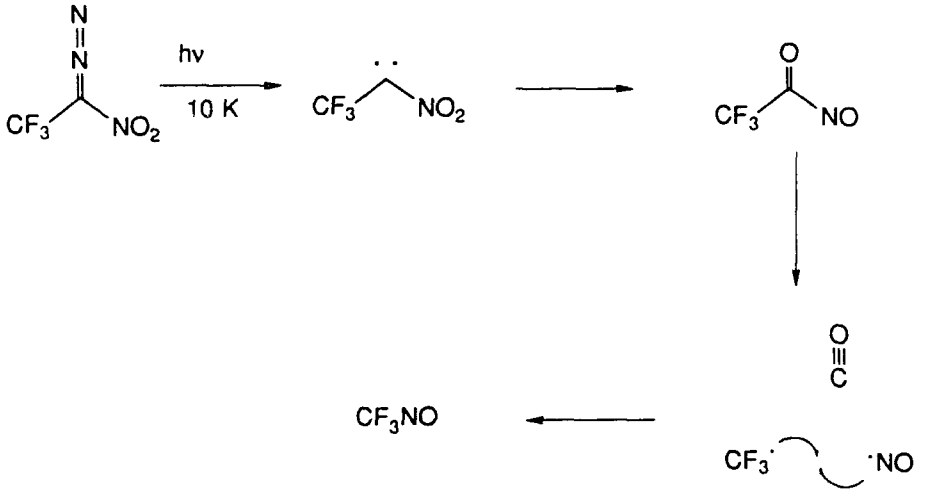
8 **12** **13**

REARRANGEMENT OF NITROCARBENES TO ACYL NITROSO COMPOUNDS

While there is still no direct spectroscopic evidence for acyl nitroso compounds such as nitrosoformaldehyde, their chemistry has been well studied by Kirby[12a,b] and exploited in synthesis by Keck.[12c] Traditionally, these highly reactive species are generated in solution by the periodate oxidation of hydroxamic acids and are trapped as eneophiles or dieneophiles. An excellent diene for the acyl nitroso Diels-Alder reaction is 9,10-dimethylanthracene. When nitrodiazomethane, ethyl nitrodiazoacetate and trifluoromethylnitrodiazomethane were treated with a catalytic amount of rhodium(II) acetate in the presence of 9,10-dimethylanthracene, Diels-Alder adducts were obtained.[13] The same adducts were also obtained under thermal conditions. This is convincing evidence that nitrocarbenes do rearrange to acyl nitroso compounds.

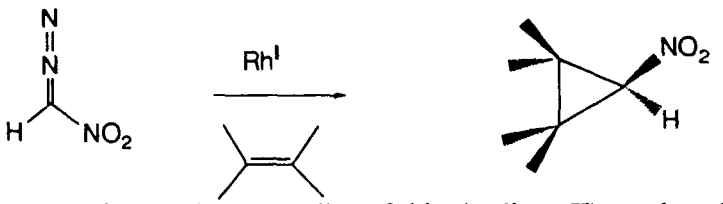


We attempted to spectroscopically observe an acyl nitroso compound under matrix isolation conditions by photolysis of an argon matrix of nitrotrifluoromethyldiazomethane at 12 K. Much to our surprise, the only product that we observed was trifluoronitrosomethane. Apparently the initially formed nitrocarbene does rearrange to the acyl nitroso compound but since this is exothermic by 100 kcal/mol, further bond cleavage takes place and carbon monoxide is eventually formed.



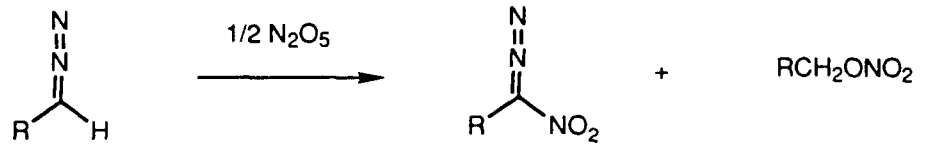
NITRODIAZOMETHANES AS PRECURSORS TO NITROCYCLOPROPANES

The transition metal mediated cyclopropanation of alkenes with diazo compounds is a valuable synthetic reaction.[14] It is especially useful in instances where the desired free singlet carbene is unstable to rearrangement.[15] Indeed, we have found that rhodium(II) acetate catalyzed decomposition of nitrodiazomethane in the presence of electron rich alkenes produces nitrocyclopropanes in useful yields.[16] The reaction works well for alkenes of all substitution patterns.[17]



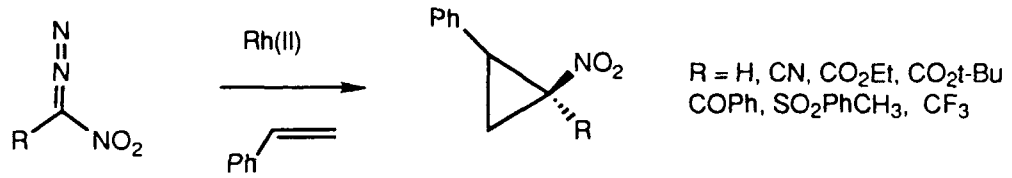
We have further investigated the generality of this rhodium(II) catalyzed cyclopropanation reaction using other substituted nitrodiazomethanes. Schöllkopf and co-workers reported the syntheses of several nitrodiazomethanes by nitration of electronegatively substituted diazomethanes

with N_2O_5.[18] The parent nitrodiazomethane is prepared by deprotection of t-butyl nitrodiazoacetate with trifluoroacetic acid followed by decarboxylation in wet methylene chloride.[19] Like nitrodiazomethane, cyanonitrodiazomethane is treacherously explosive when neat, but it can be safely and conveniently handled as the crude solution obtained from the nitration procedure. We have not experienced any problems with the purification of the other nitrodiazomethanes listed below.



R = CN
R= CO_2Et
R = CO_2t-Bu
R = (CO)Ph
R = SO_2PhCH_3
R = CF_3

Reaction of the above nitrodiazomethanes under the transition metal mediated cyclopropanation conditions with a variety of alkenes produces the 1-substituted nitrocyclopropanes.[20]



Representative examples of this reaction are shown in Table 1.

The yields of cyclopropane products depend on the structure of both the alkene and the nitrodiazo precursor. The reaction works best with electron rich, unhindered alkenes. While nitrodiazomethane and cyanonitrodiazomethane cyclopropanate all of the alkenes chosen for this study, the other nitrodiazo compounds which bear sterically demanding substituents generally do not cyclopropanate trans disubstituted and tetrasubstituted alkenes. We have recently reported a detailed study of this steric effect using ethyl nitrodiazoacetate.[21] As an example of the versatility of this method, the cyclopropanes derived from isobutylene that are available by this route are shown below.

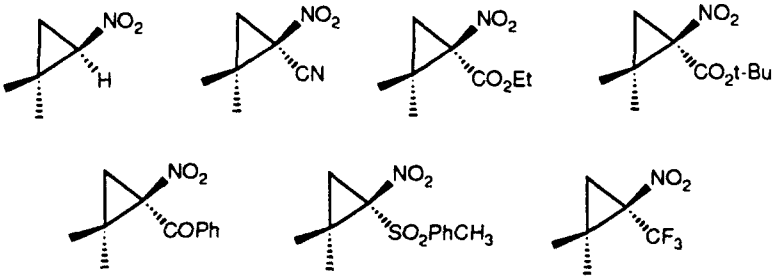
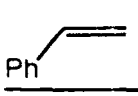
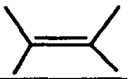


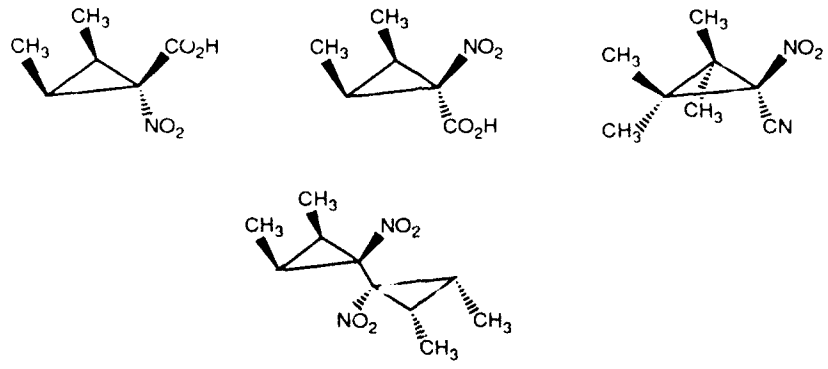
Table 1. Yields and diastereoselectivities[a] for the cyclopropanation of alkenes with several nitrodiazomethanes in the presence of rhodium(II) acetate.

						
13	54% 2.4:1	50% b	50% 1:1	30% 3:1	40% b	20% b
6	55% 2:1	50% b	40% 15:1	40% >20:1	30% b	35% b
7	75% 8:1	75% b	65% 4:1	35% 6:1	0	0
8	83% 2:1	80% b	50% 4:1	30% 4:1	c	0
9[d]	75% 1:6	58% b	45% 1:10	20% <1:20	c	0
10[d]	73% 1:2.4	72% b	53% 10:1	42% >20:1	c	0
11	30% 1:1	6% b	c	c	c	0

a. Diastereoselectivities are given as trans/cis relative to the nitro group. b. Only one diastereomer possible.
c. Reaction was not performed. d. Tentative stereochemical assignments based on NMR data from reference 10.

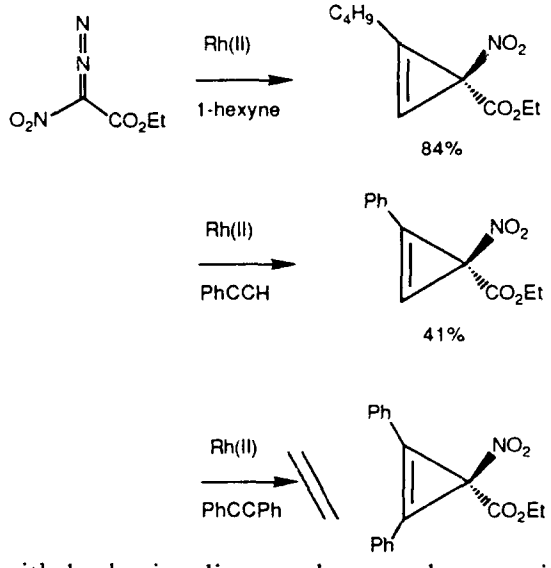
There are relatively few examples of 1-substituted nitrocyclopropanes in the literature[22, 23] and there are no general methods available for their synthesis. Our present methodology allows the ready synthesis of a variety of new 1-substituted nitrocyclopropanes in good yields from readily available starting materials. The development of this technology has been a major advance in the synthesis of nitrocyclopropanes.

We have determined the x-ray crystal structures for a number of nitrocyclopropanes,[24] some of which are shown below. The crystal densities of these compounds ranges from about 1.28 to 1.50 g/cc.

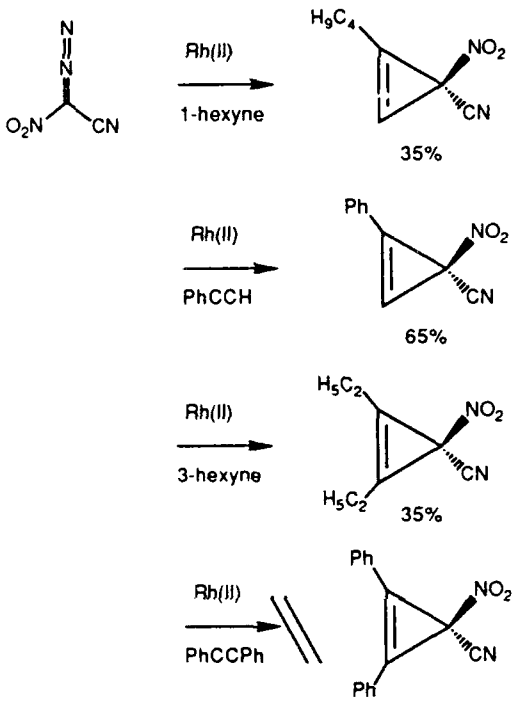


SYNTHESIS OF CYCLOPROPENES FROM NITRODIAZOMETHANES

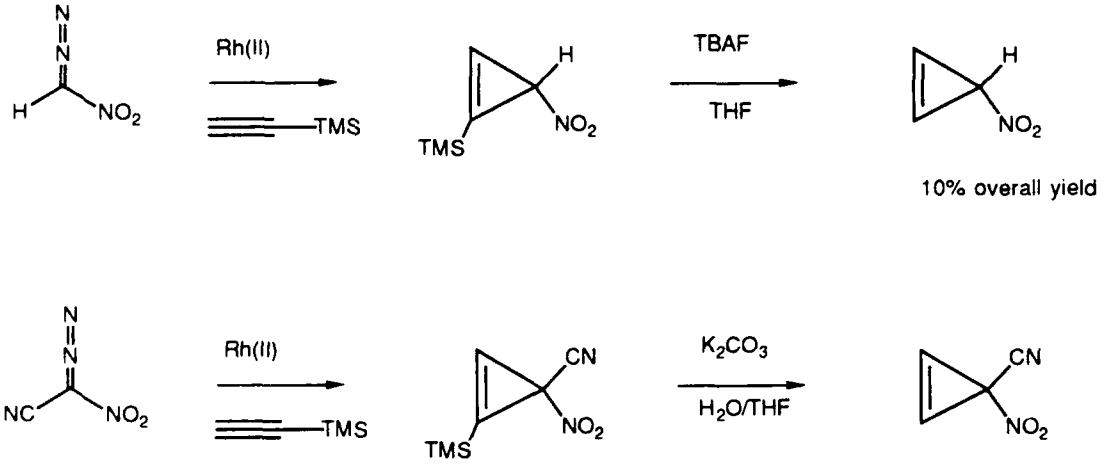
Cyclopropenes are highly energetic hydrocarbons. The parent cyclopropene has a ΔH_f of 66 kcal/mol and a strain energy of 55 kcal/mol. Addition of energetic groups such as nitro onto the nitrocyclopropene skeleton provides an opportunity to prepare even more energetic materials. To date, there is only one reported example of a nitrocyclopropene. 3-Nitro-1,2-diphenylcyclopropene was prepared by reaction of diphenylcyclopropenium ion with nitrate anion.[25] Over the past several years we have developed methodology to prepare nitrocyclopropanes using the transition metal mediated cyclopropanation of alkenes with nitrodiazomethanes.[26] Recently we have found that this cyclopropanation reaction may be extended to include alkynes. For instance, we have found that ethyl nitrodiazoacetate will cyclopropanate terminal alkynes in reasonable yields.



The reactions with both nitrodiazomethane and cyanonitrodiazomethane and terminal alkynes yield similar results. In addition, both diazo compounds will cyclopropanate some internal alkynes.

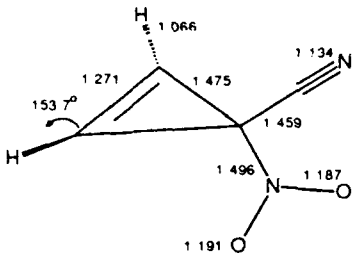


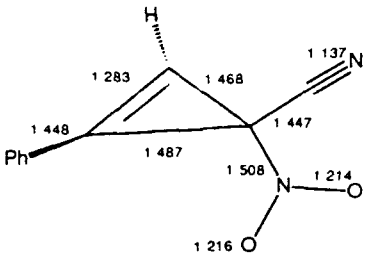
The synthesis of the parent 3-nitrocyclopropene and 3-cyano-3-nitrocyclopropene were accomplished by starting with trimethylsilylacetylene. After cyclopropanation using the appropriate diazo compound, the trimethylsilyl groups were removed to give the parent hydrocarbons.



3-Cyano-3-nitrocyclopropene is a colorless oil which is stable at room temperature for extended periods of time. Ab initio calculations (see below) predict that it will have $\Delta H_f = 90$ kcal/mol. This compound may be a useful high energy fuel.

We have obtained a crystal structure for 3-cyano-3-nitro-1-phenylcyclopropene and I have compared the X-ray structure with the ab initio HF/6-31G* optimized geometry for the parent 3-cyano-3-nitrocyclopropene. The agreement is really very good.



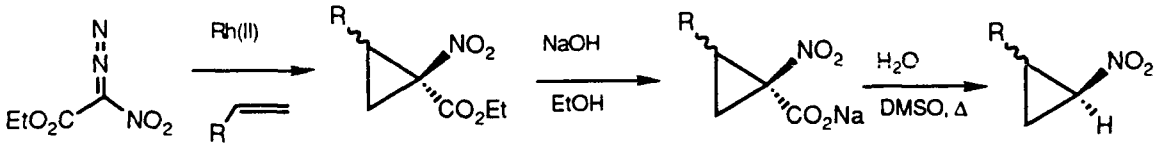


HF/6-31G*

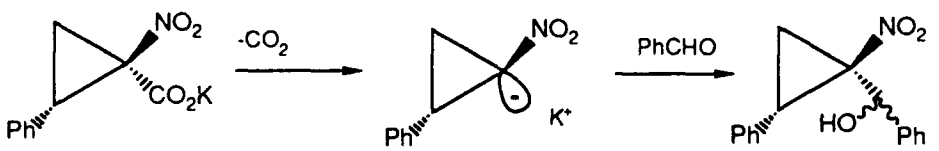
X-ray

THE CHEMISTRY OF THE NITROCYCLOPROPYL ANION

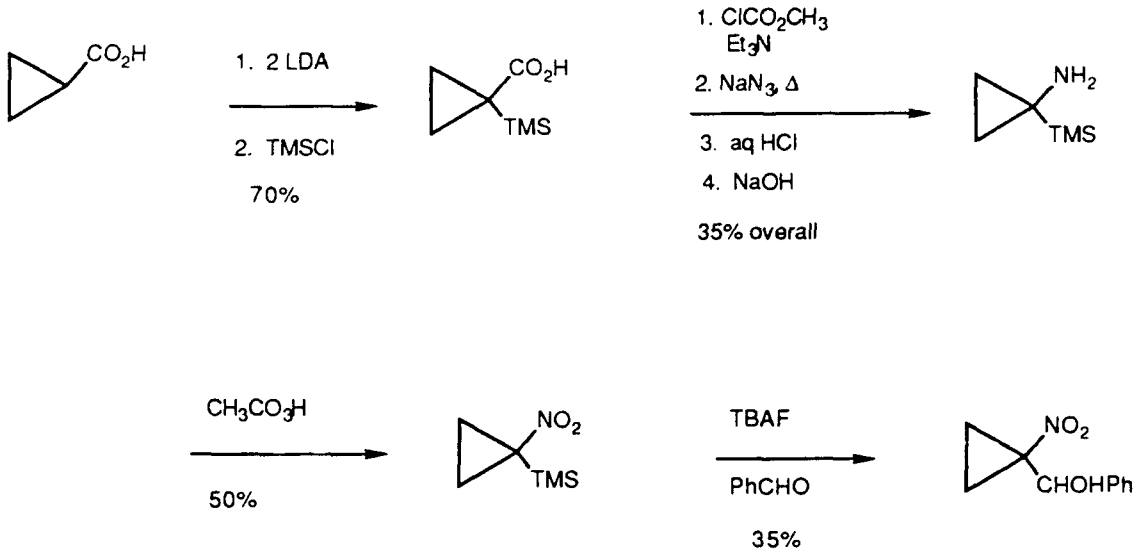
While acyclic malonic acids and β-ketoacids undergo thermal decarboxylation[27], their cyclopropyl analogs do not.[28] One of the most exciting discoveries we have made is that the sodium salts of nitrocyclopropanecarboxylic acids can be decarboxylated. The ethyl 1-nitrocyclopropanecarboxylates are easily available from ethyl nitrodiazoacetate. Saponification of the esters with sodium hydroxide at room temperature produces the sodium nitrocyclopropanecarboxylates. If these salts are heated to 80 °C under aqueous conditions, then quantitative yields of nitrocyclopropanes are produced.[29] Because of the inconvenience of its preparation and the potentially explosive nature of nitrodiazomethane, this two step method is now the method of choice for the preparation of nitrocyclopropanes substituted by hydrogen at the 1-position.



If the sodium salts are carefully dried and the decarboxylation is carried out under anhydrous conditions, the resulting nitrocyclopropyl anion can be trapped in high yields with electrophiles such as benzaldehyde.[30] Ab initio calculations predict that the nitrocyclopropyl anion is non-planar with a barrier of 3.5 kcal/mol to planarity. We have found that the decarboxylation of diastereomeric sodium 1-nitrocyclopropanecarboxylates yields different ratios of adducts with benzaldehyde depending on which diastereomer is used. More retention of configuration is observed. This is consistent with the non-planar nature of the nitrocyclopropyl anion and is the first evidence that nitrocyclopropyl anions exist as discrete intermediates.



We have developed an alternative method for the preparation of 1-nitrocyclopropyl anions and, in particular, the parent 1-nitrocyclopropyl anion. This involves fluoride ion promoted desilylation of 1-nitro-1-trimethylsilylcyclopropane. Our synthesis of this compound involves the silylation of the bisanion of cyclopropanecarboxylic acid. The acid functionality is then converted to amine via a Schmidt reaction and the amine is oxidized with peracetic acid to yield the nitro compound. The nitrocyclopropyl anion can be trapped with electrophiles such as benzaldehyde but with lower yield than the decarboxylation method.



DIAZIRINONE

AB INITIO CALCULATIONS

The synthesis of the first 3H-diazirine, the parent compound, was reported in 1960. Since that time many different diazirines have been synthesized. Diazirines are more easily made and are more thermodynamically stable than the isomeric diazo compound. Diazirines are convenient photochemical and thermal precursors to carbenes. However there is some controversy over the *thermal and photochemical reaction mechanisms of the decompositions.* There have been several theoretical studies on diazirines but all were done at a semi-empirical or non optimized ab initio level. In the present study[31], high level ab initio molecular orbital calculations were used to study both the ground states and transition structures of two known diazirines, the parent compound and difluorodiazirine. Comparison of these results with existing experimental data and similar calculations for the unknown compound diazirinone (diazacyclopropenone) allow us to make predictions about the structure and potential stability of this unusual compound. The structures and total energies of diazirine, difluorodiazirine and diazirinone calculated using the 6-31G* basis set at the SCF, MP2 and CISD levels of theory are given in Table 2. The structures of diazirine and difluorodiazirine determined experimentally by electron diffraction are included for comparison. Due to the size of the calculation, the CISD calculations were not performed for difluorodiazirine.

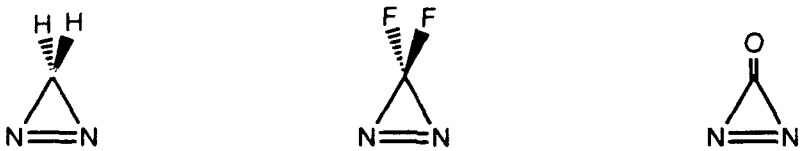


Table 2. Experimental and ab initio Total Energies, Dipole Moments and Molecular Structures for Diazirine, Difluorodiazirine and Diazirinone.

		Theoretical		
	exptl	HF/6-31G*	MP2/6-31G*	CISD/6-31G*
		Diazirine		
Dipole Moment	1.59	1.90	1.78	1.84
r(N-N)	1.228(3)	1.194	1.256	1.222
r(C-N)	1.482(3)	1.446	1.480	1.463
r(C-H)	1.09(2)	1.074	1.082	1.079
<(HCH)	117.0(20)	118.0	119.4	118.5
Total Energy		-147.8361	-148.3002	-148.2615
		Difluorodiazirine		
Dipole Moment	0.0	0.15	0.26	
r(N-N)	1.293(9)	1.230	1.306	
r(C-N)	1.426(4)	1.375	1.407	
r(C-F)	1.315(4)	1.313	1.338	
<(FCF)	111.84(52)	109.82	110.69	
Total Energy		-345.5475	-346.3491	
		Diazirinone		
Dipole Moment		1.35	0.73	1.07
r(N-N)		1.2674	1.3487	1.2953
r(C-N)		1.3473	1.3952	1.3684
r(C-O)		1.1728	1.1973	1.1850
Total Energy		-221.5179	-222.14732	-222.06559

Bond lengths in angstroms, angles in degreed, dipole moments in debye and total energy in hartrees.

Calculated bond lengths are generally too short at the Hartree-Fock level of theory but good agreement between calculated and experimental bond lengths is seen when partial electron correlation is taken into account using second order Moller-Plesset theory (MP2) or configuration interaction with all single and double substitutions (CISD). This is also true in the present case where the difference between the experimental and calculated bond lengths is generally less than 0.02 Å. Much of this difference may be due to experimental error. There is a steady change in the ring bond lengths as one moves from diazirine to difluorodiazirine to diazirinone. The nitrogen-nitrogen bond gets longer while the carbon-nitrogen bonds get shorter. One possible explanation is that diazirinone has cyclopropenium ion character and the geometrical change is due to the π system. However the same type of structural change is observed in substituted cyclopropanes. For instance, relative to cyclopropane, the carbon-carbon bond opposite the substituent in difluorocyclopropane is lengthened while the adjacent bonds are shortened. This effect is even more pronounced in cyclopropanone. The geometries of the diazirines may simply be due to a sigma effect.

It is informative to compare the enthalpies of reaction for the three diazirines decomposing to nitrogen and singlet carbene. Calculated enthalpies of reaction at the MP3/6-31G* level are shown below.

$\longrightarrow$ $N_2 + {}^1{:}CH_2$

ΔE = 40.5 kcal/mol

$\longrightarrow$ $N_2 + {}^1{:}CF_2$

ΔE = -20.5 kcal/mol

$\longrightarrow$ $N_2 + CO$

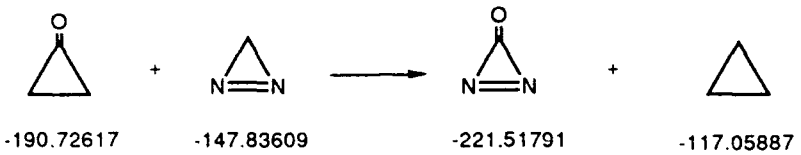
ΔE = -90.0 kcal/mol

Although there is a large change in the enthalpy of reaction between the decomposition of diazirine and difluorodiazirine, the experimental barriers to decomposition are almost the same. The enthalpy of activation for decomposition of diazirine is 33 kcal/mol and for difluorodiazirine it is 32.2 kcal/mol.

It is informative to compare the calculated electric dipole moments for the three diazirines as well as two similar compounds, cyclopropene and cyclopropenone. Calculated dipole moments at the HF/6-31G* level of theory are generally within 0.5 D of experimental values and are usually slightly higher, while those calculated at the MP2 or CISD level are usually much closer to the observed values. At the HF/6-31G* level, the values calculated for diazirine, difluorodiazirine and diazirinone are 1.91, 0.15, and 1.35 debye respectively. The experimental values are 1.59 D for diazirine and about 0.0 D for difluorodiazirine. In diazirine the nitrogen-nitrogen double bond is the negative end of the calculated dipole. However in both difluorodiazirine and diazirinone the nitrogen-nitrogen double bond is the positive end of the calculated dipole. There is clearly a large change in the charge distribution going from diazirine to difluorodiazirine to diazirinone. For comparison, the dipole moment calculated at the HF/6-31G* level for cyclopropene is 0.56 D and for cyclopropenone it is 4.69 D. The experimental values are 0.45 D and 4.39 D respectively. In both cyclopropene and cyclopropenone, the carbon-carbon double bond is the positive end of the dipole. The change in dipole moment going from diazirine to diazirinone (3.3 D) is similar to, though less than, that going from cyclopropene to cyclopropenone (4.0 D). This fact suggests that replacement of a carbonyl for a methylene group induces a similar change in the charge distributions between the two sets of compounds. Since the charge distribution of diazirinone is similar to that of cyclopropenone, one might ask whether diazirinone shows any signs of aromaticity. Some workers consider cyclopropenone to be aromatic based on its π delocalization energy. If one assumes equal strain energy on both sides of the reaction arrow, then the following isodesmic reaction, using HF/6-31G* energies, predicts that cyclopropenone has about 27 kcal/mol of delocalization energy. A similar isodesmic reaction for diazirinone predicts that it has 9 kcal/mol of delocalization energy, or only one third that of cyclopropenone. This number is similar to that obtained using a similar isodesmic reaction for the delocalization energy of methylenecyclopropene and suggests that diazirinone possesses little or no aromatic stabilization.

-190.72617 -115.82304 -189.53397 -117.05887

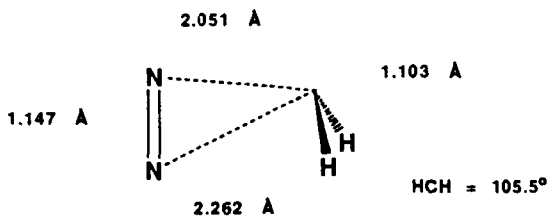
ΔE = -27.4 kcal/mol



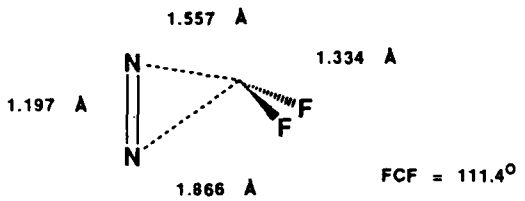
-190.72617 -147.83609 -221.51791 -117.05887

ΔE = -9.1 kcal/mol

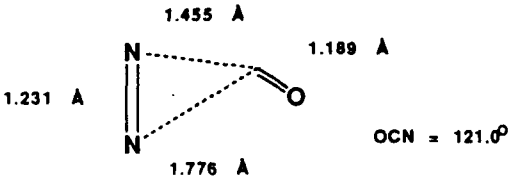
In order to determine whether diazirinone will be a unimolecularly stable species, one needs not only the ground state energy but also the energy of the transition structure. As a test of theory, the transition structures for decomposition of diazirine and difluorodiazirine to nitrogen and the corresponding carbene were also calculated at the HF/6-31G*, MP2/6-31G*, and CISD/6-31G* level. The transition structures calculated at the MP2/6-31G* level are shown below. The total energies, and calculated and experimental activation enthalpies for all three compounds are given in Table 3. From these data, diazirinone is predicted to have an experimental enthalpy of activation for decomposition to nitrogen and carbon monoxide of between 24 and 27 kcal/mol. Diazirinone should thus be an achievable synthetic target, although it will not be stable at room temperature for any length of time.



E = -148.23478 H



E = -346.28424 H



E = -222.09247 H

Table 3. Calculated and experimental activation enthalpies (kcal/mol) for decomposition of diazirines.

	$\Delta H^{\neq}$(exp)	(theoretical)		
		HF/6-31G*	MP2/6-31G*	CISD/6-31g*
diazirine	33.0	32.1	41.1	38.5
difluorodiazirine	32.2	48.7	40.7	
diazirinone		33.6	34.4	35.3

The vibrational spectrum for diazirinone was calculated at the HF/6-31G* and MP2/6-31G* levels of theory and the results are shown in Table 4. This will greatly aid in the assignment of structure when diazirinone is prepared.

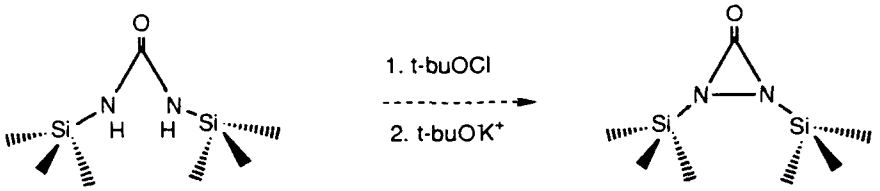
Table 4. Calculated Vibrational Spectrum for Diazirinone (cm^{-1}).

HF/6-31G*			MP2/6-31G*	
Calc.	Scaled	Int(Km/mol)	Calc.	Int(Km/mol)
2250.0	2025	682.	2085.1	353
1686.4	1518	16	1242.1	2
1170.0	1053	6	1048.2	39
1072.7	965	4	913.5	5
652.7	587	50	569.8	28
617.3	556	24	535.3	10.5

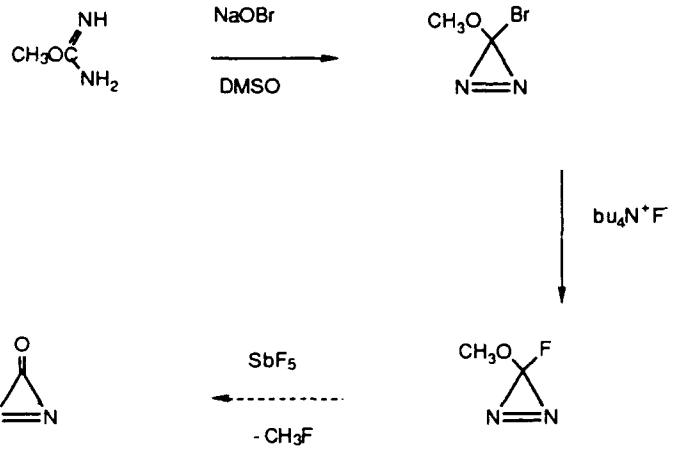
ATTEMPTED SYNTHESIS OF DIAZIRINONE

The synthesis of diazirinone was attempted using several different methods, although none were ultimately successful. Whether this is due to the inherent instability of diazirinone (and hence our calculations are quantitatively incorrect) or just the methods we have tried is unclear at this time.

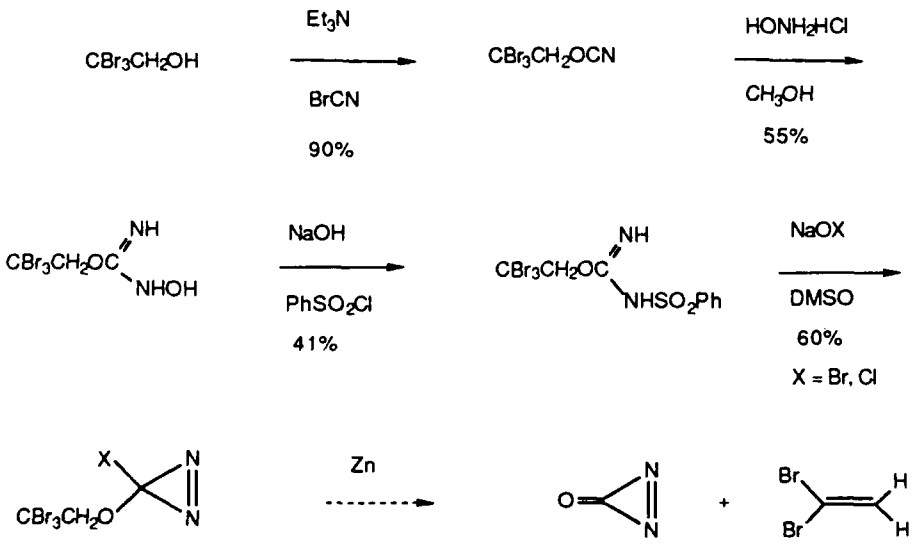
The different methods that were attempted are shown below. Our original scheme involved the synthesis of bis-trimethylsilyldiaziridinone followed by oxidative desilylation. While the synthesis of the bis-t-butyldiaziridinone was easily accomplished using this method, we were unable to prepare any of the TMS-diaziridinone using this method. Thus other methods were pursued.



Another approach to diazirinone would be the synthesis of an appropriate diazirine which could be deprotected to form the carbonyl. One method which was attempted was treatment of methoxyfluorodiazirine with antimony pentafluoride. While the diazirine could be prepared, the reaction with SbF_5 yielded no characterizable products.



Another approach involved the synthesis of a different type of protected ketal. While we were successful in preparing the precursor, we were unable to successfully generate diazirinone from it.



IR : 1545 cm^{-1} (N=N)

Although we were not successful in our quest for diazirinone, I believe that the molecule is still an achievable synthetic target.

Footnotes and References

1. (a) Schollkopf, U. and Tonne, P. "Versuche zur Erzeugung von Nitro-athoxycarbonylcarbene aus Nitrodiazoessigsaure-athylester" *Ann. Chem.* **1971**, *753*, 135. (b) Schollkopf, U. and Markusch, P. "Nitro- und Dinitrodiazomethan" *Ann. Chem.* **1971**, *753*, 143. (c) Franck-Neumann, M. and Miesch, M. "Nitrovinylcarbenes: Photolysis of the 3H-Pyrazole Precursors, Intramolecular Evolution and Intermolecular Reactivity" *Tetrahedron Lett.* **1984**, 2909. (d) Rahman, A. and Clapp, L. "Thermal Decomposition of the Potasium Salts of Dinitroalkanes" *J. Org. Chem.* **1976**, *41*, 122. (e) Coutouli-Agrgyropoulou, E. and Alexandrou, N. E. "Thermal Decomposition of the Silver Salts of Aryldinitromethanes in the Presence of Unsaturated Systems. Possible Formation of Arylnitrocarbenes" *J. Org. Chem.* **1980**, *45*, 4158.

2. Schollkopf, U.; Markusch, P. "Nitro- und Dinitrodiazomethan" *Ann. Chem.* **1971**, *753*, 143.

3. The calculations were performed using the Gaussian 82, 86 and 88 programs or GAMESS.

4. O'Bannon, P. E. and Dailey, W. P. "Nitrodiazomethane as a Source of Nitrocarbene"*Tetrahedron Lett.* **1988**, 987.

5. If one corrects for the experimental value of the singlet-triplet splitting in methylene with that calculated at a similar level of theory, then the singlet-triplet gap is close to zero.

6. See for instance, Wentrup, C. *Reactive Intermediates*, Wiley and Sons, New York, 1984.

7. (a) Regitz, M. "Recent Synthetic Methods in Diazo Chemistry" *Synthesis* **1972**, 351. (b) Regitz, M.; Maas, G. *Diazo Compounds*, Academic Press: New York, 1986.

8. Koft, E. "A One Step Preparation of α-Azido Sulfones from Nitro Compounds" *J. Org. Chem.* **1987**, *52*, 3466.

9. (a) Balli, H.; Löw, R. "Diazo-Nitro-Alkane aus Reactiven Nitroverbindungen durch Diazogruppenubertragung mit Azidiniumsalzen" *Tetrahedron Lett.* **1966**, 5821. (b) Balli, H.; Löw, R.; Müller, V.; Rempfler, H.; Sezen-Gezgin, A. "Einfuhrung der Diazogruppe in Reactive Methylenverbindungen mit Azidiniumsalzen" *Helv. Chim. Acta* **1978**, *61*, 97.

10. (a) Schöllkopf, U.; Tonne, P. "Versuche zur Erzeugung von Nitro-athoxycarbonylcarbene aus Nitrodiazoessigsaure-athylester" *Ann. Chem.* **1971**, *753*, 135. (b) Schöllkopf, U.; Markusch, P. "Nitro- und Dinitrodiazomethan" *Ann. Chem.* **1971**, *753*, 143. (c) Schöllkopf, U.; Tonne, P.; Schaefer, H.; Markusch, P. "Synthesis von Nitro-diazoessigsaureestern, Nitro-cyano- und Nitro-trifluoromethyl-diazomethane" *Ann. Chem.* **1969**, *722*, 45. (d) Frank-Neumann, M.; Miesch, M. "Nitrovinylcarbenes: Photolysis of t the 3H-Pyrazole Precursors, Intramolecular Evolution and Intermolecular Reactivity" *Tetrahedron Lett.* **1984**, 2909. (e) Rahman, A.; Clapp, L. *J. Org. Chem.* **1976**, *41*, 122. (f) Coutouli-Argyropoulou, E.; Alexandrou, N. E. "Thermal Decomposition of the Silver

Salts of Aryldinitromethanes in the Presence of Unsaturated Systems. Possible Formation of Arylnitrocarbenes" *J. Org. Chem.* **1980**, *45*, 4158.

11. O'Bannon, P. E.; Carroll, P. J.; Dailey, W. P. "Synthesis, Reactivity and Structure of Nitrodiazoacetic Acid"*Tetrahedron Lett.* **1988,** 6031.

12. (a) Corrie, J. E. T; Kirby, G. W.; Mackinnon, J. W. M. "Reactions of Transient C-Nitrosocarbonyl Compounds with Dienes, Monoolefins and Nucleophiles"*J. C. S. Perkin Trans. I* **1985**, 883. (b) Kirby, G. W. "Electrophilic C-Nitroso-compounds" *Chem. Soc. Reviews* **1977**, 1. (c) Keck, G. E.; Webb, R. R.; Yates, J. B. A Versitile Method for Carbon-Nitrogen Bond Formation via Ene Reactions of Acylnitroso Compounds" *Tetrahedron* **1981,** *23*, 4007.

13. O'Bannon, P. E. and Dailey, W. P. "Rearrangement of Nitrocarbenes to Acyl Nitroso Compounds" *Tetrahedron Lett.* **1988**, 5719.

14. Doyle, M. P. "Catalytic Methods for Metal Carbene Transformations"*Chem. Rev.* **1986**, *86*, 919.

15. Arnold, Z. "Diazoacetaldehyde as a Source of Formylcarbene: a New Carbene Species"*J. Chem. Soc., Chem. Comm.* **1967**, 299.

16. O'Bannon, P. E. and Dailey, W. P. "Nitrodiazomethane as a Source of Nitrocarbene" *Tetrahedron Lett.* **1988**, 987.

17. For other methods of preparation of nitrocyclopropanes, see:
(a) Asorskis, J.; Shecter, H. "Reactions of Conjugated Nitro Olefins with Phosphoranes and with Dimethylsulfoxonium Methylide to Give Ylides and Nitrocyclopropanes, Respectively" *J. Org. Chem.* **1968**, *33*, 1164. (b) Parham, W. E.; Braxton, H. G.; Serres, C. "Reactions of Diazo Compounds with Nitroolefins. VII. The Thermal Decomposition of Nitropyrazoles" *J. Org. Chem.* **1961**, *26*, 1831. (c) Kuwajima, I.; Ryochi, A.; Tomso, S. "Regio- and Site-Selective Activation of Carbon-Carbon Double Bonds to Nucleophilic Reagents. Cyclopropanation of Vinylselenone with Active Methylene Compounds" *Tetrahedron Lett.* **1983**, *24*, 4429. (d) Russell, G. A.; Makosza, M.; Hershbergber, J. "Synthesis of Nitrocyclopropanes by Cyclization of γ-Chloro-γ-Nitro Carboxylic Esters and Derivatives" *J. Org. Chem.* **1979**, *44*, 1195.

18. Schollkopf, U.; Tonne, P.; Schafer, H.; Markusch, P. "Synthesis von Nitro-diazoessigsaureestern, Nitro-cyano- und Nitro-trifluoromethyl-diazomethane" *Ann. Chem.* **1968**, *722*, 45.

19. O'Bannon, P. E. and Dailey, W. P. "Synthesis, Reactivity and Structure of Nitrodiazoacetice Acid" *Tetrahedron Lett.* **1988**, 6031.

20. O'Bannon, P. E. and Dailey, W. P. "The Synthesis of Nitrodiazomethanes from Nitrodiazomethanes"*Tetrahedron Lett.* **1989**,*30*, 4197-4200.

21. O'Bannon, P. E. and Dailey, W. P. "Catalytic Cyclopropanation of Alkenes with Ethyl Nitrodiazoacetate. A Facile Synthesis of Ethyl 1-Nitrocyclopropanecarboxylates" *J. Org. Chem.* **1989**,*54*, 3096 - 3101.

22. 1-Alkyl nitrocyclopropanes may be prepared by cyclopropanation of nitroolefins with dimethylsulfoxonium methylide: Asunskis, J. and Shechter, H. "Reactions of Conjugated Nitro Olefins with Phosphoranes and with Dimethylsulfoxonium Methylide to Give Ylides and Nitrocyclopropanes, Respectively" *J. Org. Chem.* **1968**, *33*, 1165.

23. For an attempted functionalization of nitrocyclopropane see: Kai, Y.; Knochel, P.; Kwiatkowski, S.; Dunitz, J. D.; Oth, J. F. M.; Seebach, D.; Kalinowski, H.-O. "Generation and Reactions of Lithiated tert-Butyl and 2,6-Di(tert-butyl)-4-methylphenylcyclopropanecarboxylates" *Helv. Chim. Act.* **1982**, *69*, 1655.

24. O'Bannon, P. E. and Dailey, W. P. "x-Ray Structural Studies of Several Novel Nitrocyclopropanes" *Structural Chemistry* **1990**, in press.

25. Cheer, C. J.; Bernstein, D.; Greenberg, A. Lyu, P. "Crystal Structure of 1,2-Diphenyl-3-nitrocyclopropene and ab Initio Calculations of 3-Nitrocyclopropene" *J. Am. Chem. Soc.* **1988**, *110*, 226-230.

26. See references 16, 19, 20 and 21.

27. (a). March, J. *Advanced Organic Chemsitry*, 3rd ed. Wiley, New York, 1985. (b). Clark, L. W. in *The Chemsitry of Carboxylic Acids and Esters*, Patai, S. ed., Wiley, New York, 1969.

28. For instance see McCloskey, C. M.; Coleman, G. H. "Cyclopropanecarboxylic Acid" *Organic Syntheses, Coll. Vol. 3*, Wiley, New York, 1955, p. 221 and ref 4b.

29. O'Bannon, P. E. and Dailey, W. P. "The Decarboxylation of Sodium 1-nitrocyclopropanecarboylates. A Facile Synthesis of Nitrocyclopropanes" *J. Org. Chem.* **1990**, *55*, 353-355.

30. O'Bannon, P. E. and Dailey, W. P. "Generation and Reactivity of the 1-Nitrocyclopropyl Anion" *J. Am. Chem. Soc.* **1989**, *112*, 9244-9245.

31. Portions of these results have been published: J. A. Berson, D. M. Birney, W. P. Dailey and J. F. Liebman "Ethylenedione, Its Ions and Isoelectronic Analogs" in "Molecular Structure and Energetics", J. F. Liebman and A. Greenberg, Eds., VCH Publishers, Vol. 6, 1988.