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NITROCYCLOPROPANES FROM NITRODIAZOMETHANES. PREPARATION AND REACTIVITY

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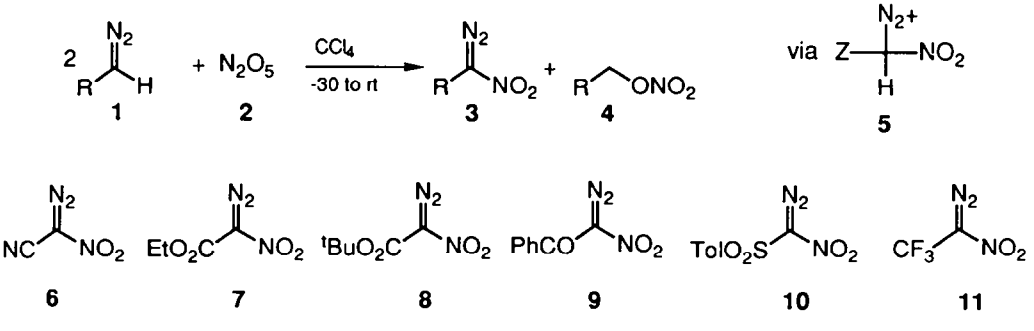
Abstract: Nitrodiazo compounds cyclopropanate electron rich alkenes in the presence of rhodium(II) acetate. The yields and diastereoselectivities are dependent on both the alkene and the nitrodiazo precursor. Nitrocyclopropanecarboxylates undergo ring opening, reduction and hydrolysis.

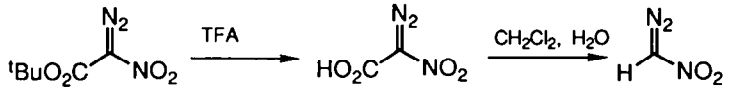
There has recently been considerable effort directed at the synthesis and study of strained ring nitro compounds as high-energy density materials.[1] Nitrocyclopropanes are the simplest members of this class of compounds. Although there are several preparative methods for nitrocyclopropanes,[2] an obvious choice, the addition of a nitrocarbene to an olefin has only recently been described by us.[3] In fact, despite the wealth of information on carbenes,[4] there are only a handful of publications on nitrocarbenes.[5]

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.[6] This reaction, unfortunately, is not applicable to nitro compounds.[7] An azidinium salt will transfer a diazo group to methyl nitroacetate and nitroacetophenone.[8] Attempts to extend this method to nitromethane or other nitro compounds were unsuccessful.[8b]

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.[5c] 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.[3c,5c]

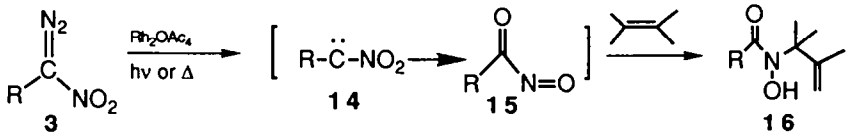


The application of this procedure to diazomethane or phenyl diazomethane failed. Presumably the intermediate diazonium ion **5** loses nitrogen before deprotonation occurs. The parent nitrodiazomethane (**13**) is prepared by deprotection of the t-butyl ester **8** with trifluoroacetic acid and proceeds via nitrodiazoacetic acid (**12**).[9]



8 **12** **13**

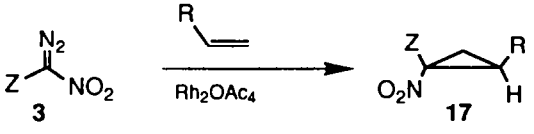
Photolysis or thermolysis of nitrocarbene precursors **7** and **13** in the presence of 2,3-dimethyl-2-butene afforded no nitrocyclopropanes and no other trapping products indicative of a nitrocarbene.[5a,b] Recent *ab initio* calculations predict that if free singlet nitrocarbene is ever formed, it will rearrange to nitrosoformaldehyde (**15**, R = H).[3a] This prediction has received experimental support.[10] Nitrosoformaldehyde is the simplest member of a class of reactive intermediates known as acyl nitroso compounds. These compounds engage in an ene reaction with alkenes and a Diels-Alder reaction with 1,3 dienes.[11] When nitrodiazo compounds **7, 8, 11** and **13** are heated in the presence of an alkene, n-alkylhydroxamic acids **16** are obtained which result from an ene reaction. Trapping with 9,10-dimethylanthracene affords Diels-Alder adducts.[10]



3 **14** **15** **16**

R = H, EtO_2C, $^tBuO_2C$, CF_3

The transition metal mediated cyclopropanation of alkenes with diazo compounds is a valuable synthetic reaction.[12] It is especially useful when the desired free carbene is unstable to rearrangement. For instance, formyl carbene undergoes Wolff rearrangement to ketene rather than addition to olefins, but the copper catalyzed decomposition of formyldiazomethane in the presence of olefins yields cyclopropanes.[13] In a preliminary communication[3c] we reported the successful application of this method to the preparation of nitrocyclopropanes **17** from nitrodiazomethanes **6-11** and alkenes. We have already described in detail the reaction between ethyl



3 **17**

Z = H, EtO_2C, $^tBuO_2C$, CN, Tosyl, PhCO, CF_3

nitrodiazoacetate (**7**) and a number of alkenes of differing electronic and steric demand.[3b] In that work it was shown that rhodium(II) acetate will transfer nitrocarbethoxy carbene to electron rich, sterically undemanding alkenes. The reaction works well with styrene and geminal and cis disubstituted alkenes. Trans and tetrasubstituted alkenes generally do not yield nitrocyclopropanes. A comparison of the reactivity of **7** and ethyl

diazoacetate indicated that **7** was significantly more sensitive to both the steric and electronic nature of the reactant alkene. Doyle's model[14] for catalytic cyclopropanations with rhodium(II) acetate was used to explain the experimental observations.

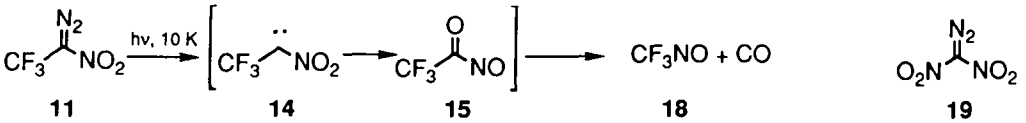
In this contribution we provide experimental procedures for the nitration of diazo compounds, discuss the remarkable selectivities observed in the cyclopropanation of alkenes with nitrodiazo compounds and report some simple reactions of these densely functionalized molecules.

Results and Discussion

Nitrodiazoalkanes: Some Properties and a Matrix Experiment

During the course of the past years we have gained considerable experience in working with compounds **6-13**. We have introduced a few modifications that simplify the original nitration procedure. These compounds exhibit varying stability, ranging from nearly benign to highly explosive. The nitrodiazo esters are the most pleasant to work with, for they may be prepared on a decagram scale and are easily purified by flash chromatography. The neat compounds may be stored for many months at 5 °C. Schöllkopf reports that nitrodiazoacetonitrile (**6**) in its pure state is extremely explosive. We have never purified this material, but find that the crude mixture obtained from the nitration reaction can be handled and stored with relative ease. Importantly, this impure material also undergoes the cyclopropanation reaction. Nitrodiazoacetic acid (**12**) and nitrodiazomethane (**13**) have exploded violently on several occasions and should be handled with extreme caution. Nevertheless, if a few points are kept in mind, both compounds may be prepared in 0.5 to 1.0 g quantities without undue fear or worry. Our experience with the nitrodiazosulfone **10** and nitrodiazoketone **9** is limited, however, nitrodiazoacetophenone (**9**) can be purified by recrystallization and stored for a few weeks in a freezer. In keeping with the propensity of diazosulfones to lose nitrogen at ambient temperature, **10** also exhibits this behavior.

A particularly interesting species is trifluoromethylnitrodiazomethane (**11**). Its relative stability with regard to detonation and its volatility make it an attractive candidate for matrix isolation experiments. With the hope of spectroscopically observing either a nitrocarbene or its acyl nitroso isomer, **11** was deposited in an argon matrix at 12 K. After irradiation of the diazo species ($\lambda > 220$ nm) the characteristic IR bands for the diazo and nitro groups had disappeared and new bands had grown in. After comparing this spectrum with that of authentic trifluoronitrosomethane (**18**),[15] we were able to assign the new bands to this compound and carbon monoxide. Clearly, a lot of chemistry is occurring in this cryogenic environment. We postulate that the initially formed nitrocarbene undergoes rearrangement to the acyl nitroso compound. For the parent nitrocarbene this oxygen migration is calculated to have no activation barrier and to be exothermic by 100 kcal/mol.[3a] Fragmentation of chemically activated **15** and recombination of CF_3 and NO affords the observed products. Alternatively, the intermediate acyl nitroso species could undergo photochemical extrusion of CO. Additional experiments employing a monochromatic light source and different matrix media may aid in distinguishing which process is operative. In the gas phase at room temperature **11** rearranges to **18** with a half-life of about 2 hours.

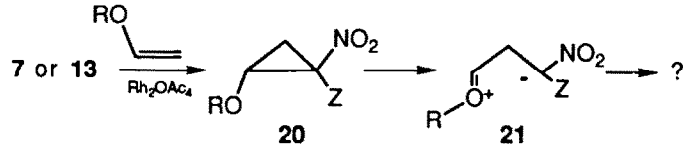


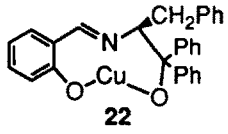
11 **14** **15** **18** **19**

Dinitrodiazomethane (**19**) is potentially accessible via the nitration of nitrodiazomethane (**13**). In fact Schöllkopf and Markusch have reported this transformation.[5b] We, however, could not prepare this species.

Catalytic Cyclopropanation of Alkenes with Nitrodiazo Compounds

All of the nitrodiazocompounds **6-13** do cyclopropanate electron rich alkenes in the presence of a catalytic (0.5 - 3 mol%) amount of rhodium(II) acetate. The results from the cyclopropanation of various alkenes are presented in Table 1. Electron poor alkenes such as vinylidene chloride and ethyl acrylate do not yield cyclopropanes. This is consistent with results from other rhodium(II) catalyzed cyclopropanations.[12] Vinyl ethers, which are the most reactive alkenes toward diazo esters, do not afford nitrocyclopropanes with **7** and **13**. We have been unable to characterize any material from these reactions, but based on the chemistry of related cyclopropanes,[16, 17] we speculate that the incipient push-pull cyclopropanes **20** undergo ring opening. The





ultimate fate of the zwitterionic species **21** is unknown. While numerous transition metal complexes are known to catalyze the cyclopropanation of alkenes,[18] our studies have centered on rhodium(II) acetate. We briefly examined reactions employing $Cu(OAc)_2$ and the chiral copper complex **22**[19] as catalysts. The yields of nitrocyclopropanes were markedly lower with both of these catalysts. The material obtained using the chiral catalyst did exhibit optical activity, but the optical purity was not determined. Because the copper catalyzed reactions are carried out at an elevated temperature and nitrodiazo compounds are thermally quite labile,[20] thermal decomposition of the diazo compound results in diminished yields.

From the data displayed in Table 1 it is immediately apparent that the yield and stereoselectivity of the cyclopropanation reaction varies widely with the alkene and the nitrodiazo precursor. The reaction works best with electron rich, unhindered alkenes. While **13** and **6** cyclopropanate all of the alkenes chosen for this study, **7-10**, which bear sterically demanding substituents, generally do not cyclopropanate trans and tetra substituted alkenes. Moreover, there is a decrease in yield in proceeding down the columns from isobutene to cyclohexene. In a detailed study of the reaction between **7** and 13 alkenes, a linear correlation between olefin reactivity and yield of cyclopropane was established.[3b] We concluded that if the alkene was not reactive, the nitrocarbethoxy carbene dissociated from the metal and rearranged to its acyl nitroso isomer. This species then decomposed or underwent an ene reaction with the alkene (Scheme I). While ene products have not been observed in the reactions of **6, 9** and **10**, the data suggest the operation of a similar mechanism .

For the most part, when mixtures of isomers are formed a chromatographic separation is not possible. The exceptions are phenyl substituted cyclopropanes and nitrocyclopropanes derived from nitrodiazomethane. The ethyl esters obtained from **7** can be separated by selective saponification.[3b] Fortunately, in most other cases the diastereoselectivity is good.

Table 1. Yields[a] and Diastereoselectivities[b] for the Cyclopropanation of Alkenes with Nitrodiazomethanes **6-13**.

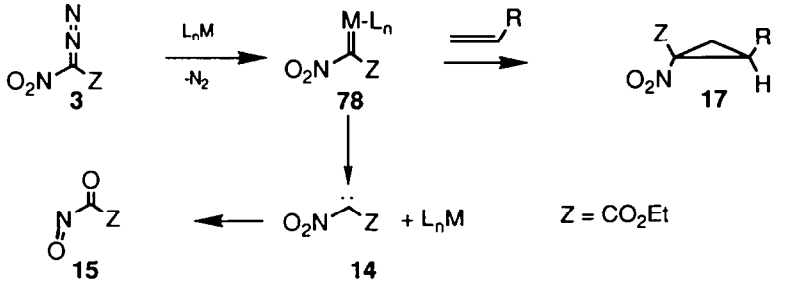
	13			**6**[c]			**7**[d]			**8**			**9**			**10**		
	%	t/c	Nr	%	t/c	Nr	%	t/c	Nr	%	t/c	Nr	%	t/c	Nr	%	t/c	Nr
styrene	54	2.4	**23,24**	55	3.0	**34,35**	75	8.0	**43,44**	83	2.0	**52,53**	75	.16	**57**	73	.42	**62,63**
isobutene[e]	50		**25**	50		**36**	75		**45**	80		**54**	58		**58**	72		**64**
1-hexene	50	1.4	**26,27**	55	3.0	**37,38**	35	1.0	**46,47**									
cis-2-butene	50	1.0	**28,29**	40	15	**39**	65	4.0	**48,49**	59	4.0	**55**	45	.10	**59,60**	53	10	**65**
cyclohexene	30	3.0	**30,31**	40	>20	**40**	35	6.0	**50,51**	30	4.0	**56**	20	>.05	**61**	42	>20	**66**
2,3-dimethyl-2-butene[e]	35		**32**	35		**41**	0[f]			0[f]			0			0		
trans-2-butene[e]	40		**33**	30		**42**	0[f]											

[a]Yields are based on isolated material. When isomeric mixtures are obtained only those isomers that could be fully characterized are assigned a number (Nr). [b]Diastereoselectivities are given as trans/cis (t /c) relative to the nitro group. The first number (Nr) refers to the major isomer. [c]Combined yield for the nitration and cyclopropanation steps. [d]Taken from reference 3b. [e]Only one isomer possible. [f]An ene product accounted for ca. 80% of the material.

Notes

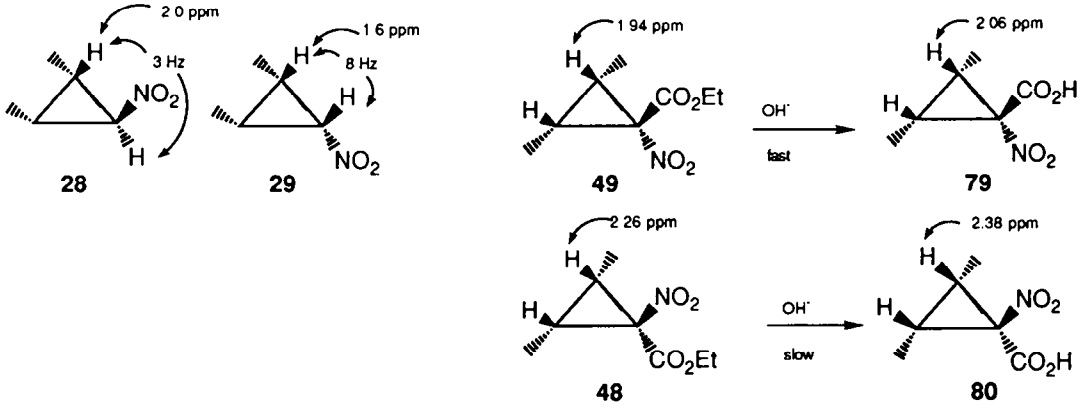
1. Vinyl acetate is cyclopropanated by nitrodiazomethane (**13**) (50%; 1.1:1; **67, 68**) and ENDA (**7**) (55%; 3:1; **69, 70**).
2. Trifluoromethylnitrodiazomethane (**11**) cyclopropanates styrene (30%, 1:1, **71, 72**), isobutene (6%, **73**), vinyl acetate (15%, 1:1, **74, 75**).
3. Methyl nitrodiazoacetate (**76**) cyclopropanates styrene (70%, >10:1, **77**).
4. Nitrodiazoacetic acid (**12**) affords nitrocyclopropanes **23-33** in this reaction.

Scheme I



Diastereoselectivity of the Cyclopropanation

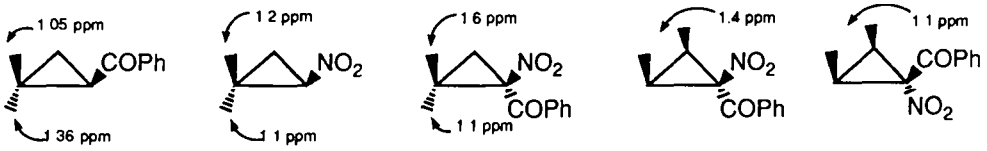
The relative ratios of diastereomeric products obtained in the cyclopropanation reaction are determined by integration of the peaks corresponding to the cyclopropyl protons in the ^{1}H NMR spectrum. In nearly all cases, the spectra of mixtures of isomers showed distinct sets of cyclopropyl hydrogens or cyclopropyl methyl groups. The accuracy of the stereochemical assignment has a direct bearing upon the following interpretation of these results. In cyclopropanes derived from **13**, cyclopropyl protons syn to the nitro group appear ca. 0.4 ppm downfield relative to trans protons. The 3 Hz coupling constant observed for **28** and the 8 Hz coupling constant in **29** support the notion that the nitro group deshields cis protons relative to trans protons. The NMR evidence alone does not allow one to be certain of the geometries of cyclopropanes derived from other nitrodiazo compounds. Nitrocyclopropanecarboxylates derived from esters **7** and **8** consistently show cyclopropyl hydrogens separated by ca. 0.2 ppm. It was thought that hydrogens syn to the nitro group should appear farther downfield than hydrogens



syn to the carboxylate group. While the rates of hydrolysis of the diasteromeric esters **48** and **49** support this belief, confirmation comes from X-ray structure data for the carboxylic acids **79** and **80**.[21] Thus a nitro group is more effective in deshielding syn cyclopropyl hydrogens than a carboxylate group.

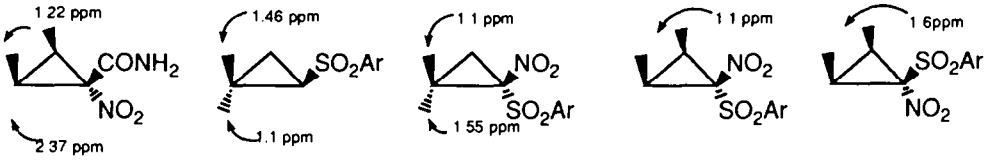
This information does not immediately permit one to assign the stereochemistry of cyclopropanes derived from **6, 8, 9** and **10**. If we make the reasonable assumption that the deshielding ability of a carboxylate group is not significantly different from other carbonyl compounds, then we can assign the stereochemistry of the benzoyl

nitrocyclopropanes. This assumption can be checked by comparing the chemical shifts of the methyl groups of model compounds **81**,[22] **25**, **58**, **59** and **60**. Although a benzoyl goup deshields cis protons relative to trans protons, cis methyl groups are shielded relative to trans methyl groups.



81 **25** **58** **59** **60**

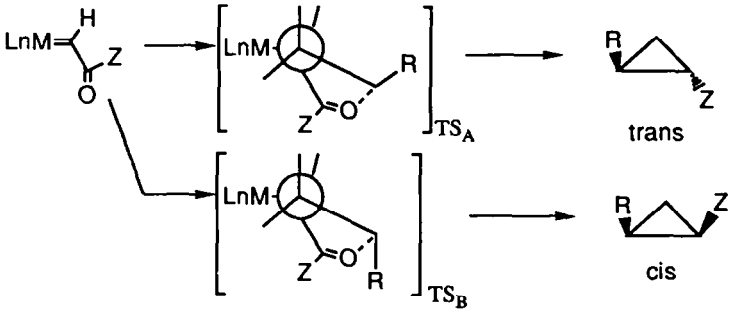
The question of stereochemical assignment becomes somewhat clouded in the case of sulfonyl cyclopropanes and nitrocyclopropanecarbonitriles, because the cyclopropyl hydrogens in mixtures of isomers sometimes overlap and often only one isomer can be detected in the ^{1}H NMR spectrum of the mixture. The assignment of stereochemistry for nitriles is based on the hydrolysis product **82** from **39**. The chemical shifts of the methyl groups and the hydrogens are more consistent with a trans orientation of the nitro group. The stereochemistry of the sulfones is based on the chemical shifts of the methyl groups in compounds **25**, **83**,[23] **84**, **64** and **65**. From this collection we state that the sulfonyl group is more effective than a nitro group in deshielding both syn cyclopropyl hydrogens and methyl groups.



82 **83** **64** **84** **65**

The range of selectivities observed from the cyclopropanation of alkenes with **6-13** is quite broad and not immediately very informative. With the aid of Doyle's model[14] for catalytic cyclopropanation reactions, some trends in Table 1 can be discerned and understood. Reactions between diazoacetates or diazoamides and alkenes where a rhodium(II) catalyst is used exhibit a preference for trans products.[24] This trans preference has been attributed to stabilization of the electrophilic β carbon by the carbonyl group (Scheme II). Because of the greater nucleophilicity of the amide carbonyl group, this trans preference is stronger for amides than esters. Steric bulk also favors trans product formation. This effect is most pronounced with bulky amides and to a lesser extent with bulky esters. Greater trans selection is also observed for alkenes bearing large groups. Undoubtably, this is due to steric repulsion between the ester or amide moiety and alkene substituents in the transition state leading to cyclopropanes (transition state A is favored over transition state B). By varying the ligands on the rhodium center, the electrophilicity of the carbenoid can be tuned, and it has been found that electron donating ligands on the metal enhance trans selectivity while electron withdrawing ligands reduce trans selectivity.

Scheme II



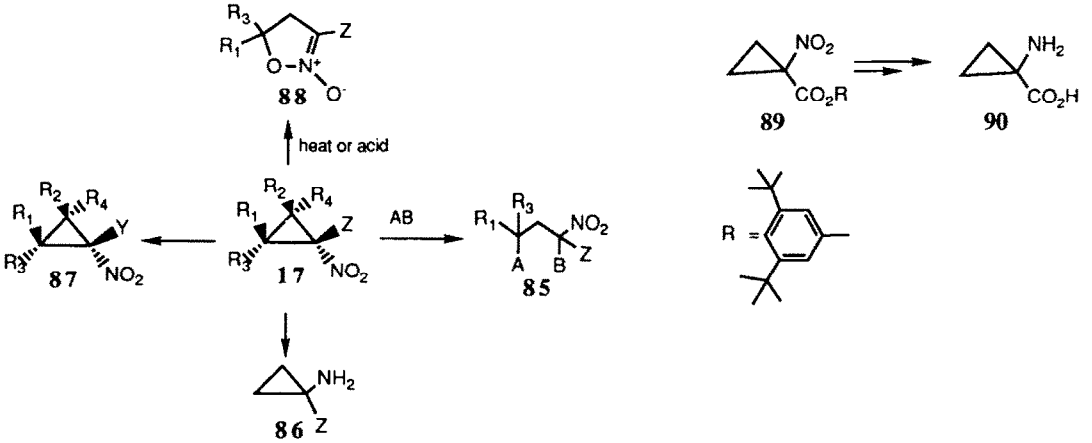
Most of the data in Table 1 can be explained in terms of these steric and electronic influences. In the product nitrocyclopropanes **17** the nitro group most often prefers a trans orientation relative to alkene substituents. In a previous study of the cyclopropanation of alkenes with **7**[3b] we attributed this reversal of stereochemical preference to the greater nucleophilicity of the nitro group relative to the carboxylate carbonyl. The increased electrophilicity of the carbenic carbon due to the nitro group may also play a role in this reversal of selectivity. The ethyl ester **7** is slightly more discriminating than the t-butyl ester **8**. As the size of the ester increases, steric interactions between the ester and the alkene will become more important, and consequently a greater proportion of the products will have the ester and alkene groups in a trans relationship. Still greater trans selectivity is obtained in the reaction between methyl nitrodiazoacetate (**76**) and styrene (>10:1). The trans orientation of the nitro group is most pronounced for cyclopropanes derived from nitrodiazoacetonitrile (**6**). The nitrile moiety is smaller than an ester group and steric factors favoring a trans orientation of the nitrile unit will be correspondingly small. The nitrile function is non-nucleophilic and will not exert any electronic directing influence on the alkene. Conversely, the size and the electronics of the benzoyl group in nitrodiazoacetophenone (**9**) act cooperatively to direct the benzoyl group to a trans position on the cyclopropane ring. That is, the nucleophilic benzoyl oxygen and the size and proximity of the phenyl group to the carbenic center outweigh the directing power of the nitro group. We could not have predicted this result; we only rationalize it in these terms.

The results from toluenesulfonylnitrodiazomethane (**10**) appear to contradict the foregoing argument. Both the size and the basicity of the tosyl group should direct it trans. Instead, most often the nitro group assumes a trans orientation. It may be that for a group to exert an electronic directing influence it should be sp^2 hybridized. Nitrodiazomethane (**13**) is the least sterically discriminating of the compounds studied here. We expected this compound to exhibit the greatest selectivity, because there is no competing steric or electronic presence to favor cis product formation. Perhaps two electron withdrawing groups are necessary for enhanced selectivity. Clearly, more experiments are needed to pin down the magnitude and origin of the steric and electronic factors that govern the selectivities observed in the metal catalyzed cyclopropanation of alkenes with diazocompounds, particularly disubstituted diazocompounds.

Reactions of Nitrocyclopropanes

There are three different sites available for chemical modification in these molecules: the nitro group, the substituent Z and the cyclopropane ring. Häner and Seebach have reported the reduction of the parent nitrocyclopropane carboxylate **89** to the amine by catalytic hydrogenation at medium pressure for 48 h.

Subsequent hydrolysis and deprotection furnished aminocyclopropanecarboxylic acid (**90**) in very good yield.[25] The use of a bulky ester group,[26] precluded hydrolysis or reduction to intact nitrocyclopropyl acids or nitrocyclopropane methanols. Seebach has also described a variety of nucleophilic ring opening reactions of **89**.[27]



The results of ring opening reactions of ethyl esters obtained from **7** are presented in Table 2. Not only do nucleophiles open the ring (entries 1-3), but the presence of cationic stablilizing groups (phenyl, gem dimethyl) facilitates electrophilic ring opening (entries 4-6). When these compounds are heated or treated with an acid, they isomerize to isoxazoline N-oxides **88**[28] (Table 3). For instance, stirring cyclopropane **45** with $BF_3{\cdot}Et_2O$ for 1 h at room temperature effects quantitative isomerization. In certain cases silica gel promotes the reaction. Alternatively, the isomerization may be achieved by heating the compound in DMSO. In all of these reactions, ring opening occurs exclusively across the more highly substituted bond. This same regioselectivity has been observed by Danishefsky for **91**[29] and is consistent with the solvolysis studies by Cram on **92**.[30]

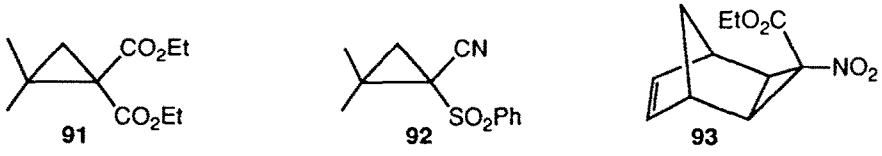


Table 2. Ring opened products **85** (Z = CO_2Et)

Entry	R_1	R_3	A	B	Yield	Nr
1	Ph	H	CN	H	41%	**94**
2	Ph	H	PhNH	H	95%	**95**
3	Me	Me	MeO	H	96%	**96**
4	Me	Me	Br	Br	36%	**97**
5	Ph	H	Br	Br	100%	**98**
6	Me	Me	$OCCF_3$	H	67%	**99**

Table 3. Isoxazoline N-oxides **88**

R_1	R_3	Z	Nr
Me	Me	CO_2Et	**100**
Ph	H	CO_2Et	**101**
Ph	Ph	CO_2Et	**102**
Ph	H	CN	**103**
Ph	Me	COPh	**104**

Some simple transformations of the ester and nitrile units of cyclopropanes derived from **6** and **7** are presented in Table 4. All of the ethyl esters can be saponified to the corresponding sodium carboxylates. The saponification should be conducted at room temperature, for attempts to increase the rate of hydrolysis by heating resulted in greatly diminished yields. In most cases, hydrolysis is complete in 1 to 16 h, although the extremely hindered ester **93** requires 10 days. Thermal decarboxylation of these salts affords nitrocyclopropanes in excellent yield.[31] When solutions of carboxylates obtained from **44** and **45** (entries 4 and 5) were acidified, no nitrocyclopropanecarboxylic acids could be isolated. On the other hand, intact carboxylic acids were obtained from **48, 49** and **50** (entries 1, 2, 3). The increased acid lability associated with the gem dimethyl and phenyl groups prevents the isolation of acids in the cases of entries 4 and 5. Similarly, the nitriles from **6** undergo hydrolysis with varying degrees of success (entries 6-8). The yield of amide decreases with increasing substitution of the cyclopropane ring. We suspect that nucleophilic ring opening by hydroperoxide ion begins to compete with amide hydrolysis as the nitrile moiety becomes more sterically encumbered. The last entry in Table 4 demonstrates that the ethyl esters from **7** can be smoothly reduced by LAH to nitrocyclopropane methanols.

Table 4. Hydrolysis and Reduction Products **87** of Cyclopropanes **17**.

Entry	R_1	R_2	R_3	R_4	Z	Y	Yield	Nr
1	Me	Me	H	H	CO_2Na	CO_2H	95%	**80**
2	H	H	Me	Me	CO_2Na	CO_2H	95%	**79**
3	$-(CH_2)_4-$		H	H	CO_2Na	CO_2H	67%	**105**
4	Me	H	Me	H	CO_2Na	CO_2H	0%	
5	Ph	H	H	H	CO_2Na	CO_2H	0%	
6	Me	Me	Me	Me	CN	$CONH_2$	26%	**106**
7	Me	Me	H	H	CN	$CONH_2$	46%	**82**
8	n-Bu	H	H	H	CN	$CONH_2$	75%	**107**
9	Me	H	Me	H	CO_2Et	CH_2OH	83%	**109**

Concluding Remarks

The nitration of diazo compounds provides a number of chemically interesting compounds. In this contribution we have described one aspect of their chemistry. The cyclopropanation of alkenes with nitrodiazo compounds has made accessible a variety of densely functionalized molecules. While this method is not without its limitations, it is by far the most versatile method for the preparation of nitrocyclopropanes. The extension of this method to the preparation of other strained nitro substituted compounds such as cyclopropenes and bicyclobutanes[32] should provide new high-energy density materials. Particularly significant is the ability to prepare nitrocyclopropanes with substituents at the position α to the nitro group. The nitrocyclopropyl anion is not well suited to electrophilic capture,[33] and the nitration of substituted cyclopropanes suffers from severe limitations.[26] In view of the importance of amines, amino acids, amino alcohols, cyclopropyl amines and cyclopropyl methanols in biochemistry,[34] reduction of the nitro group should provide a number of biologically interesting compounds. Ring opening followed by reduction of the nitro group and cleavage of the ester affords free amino acids.[27] Thus the nitrocyclopropyl esters correspond to 2-aminobutanoic acid a^4 synthons.[35] The

detailed experimental procedures that follow are the results of our experience with these compounds over the past several years and are intended to make these compounds more accessible.

Experimental Section

General methods. Proton magnetic resonance spectra were obtained in $CDCl_3$ with Bruker AM250, AC250, WP 200 and AM500 spectrometers. Chemical shifts are reported in δ units with $CHCl_3$ as an internal standard at 7.20 ppm. Carbon 13 magnetic resonance spectra were obtained with a Bruker AM500 spectrometer set at 125 MHz. Chemical shifts are reported in δ units with $CDCl_3$ as an internal standard at 77.0 ppm. High resolution mass spectra were obtained on a VG-ZAB-E mass spectrometer under ammonia chemical ionization conditions. Infrared spectra were obtained on a Perkin-Elmer 1430 instrument as thin films for oils and as methylene chloride films for solids. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. Melting points were carried out in open capillary tubes on a Meltemp aparatus and are uncorrected. Flash chromatography (fcc) was on Silica Gel 60 from Fluka. Thin layer chromatography was carried out on F-254 silica gel 60 plates obtained from E. Merck, Darmstadt. These plates were visualized with a UV lamp. In cases where cis/trans mixtures of products were obtained mass and infrared spectral data are listed only for the major isomer.

CAUTION: Nitrogen dioxide and dinitrogen pentoxide are extremely toxic and hazardous substances. All diazo compounds and particularly nitrodiazo compounds are potentially toxic and explosive. **Nitrodiazoacetic acid (12) and nitrodiazomethane (13) are extremely explosive.** A face shield and heavy gloves should be worn when working with these two compounds.

General comments on the dinitrogen pentoxide nitration of electronegatively substituted diazocompounds. The procedures given below are detailed modifications of the original Schöllkopf procedures.[5a] Diazo esters are nitrated in reagent grade CCl_4 at -30 °C and are purified by fcc. The other diazo compounds are nitrated in reagent grade CH_2Cl_2 at -78 °C. In all nitrations it is most important that the N_2O_5 be pure and that the diazo compound be dry.

Dinitrogen Pentoxide (N_2O_5).[36] The following procedure should be carried out in a well ventilated hood. Nitrogen dioxide (10 to 40 g) is condensed into a 2 neck 500 ml round bottom flask (rbf). A stream of ozone is passed over the solid NO_2 and NO_2 is slowly allowed to thaw. Ozone and nitrogen dioxide react in the gas phase to produce N_2O_5 which is collected in a U-trap at -78 °C. The other end of the trap is sealed with a Drierite drying tube. In 4 to 6 hours 10 to 20 g of N_2O_5 will have collected in the trap. This material is then vacuum transferred to a tared and flame dried 500 ml 1 neck rbf before use. N_2O_5 may be kept indefinitely at temperatures below -30 °C. Above this temperature it dissociates to nitrogen dioxide and oxygen.

Ethyl Nitrodiazoacetate (ENDA) (7). Ethyl diazoacetate (EDA) was prepared according to an Organic Syntheses procedure[37] and used as 60-85 wt % solutions (judged by NMR) in CH_2Cl_2. A solution of EDA in CH_2Cl_2 (56 g, 0.49 mol. as a 66 wt % solution) was dissolved in 400 ml CCl_4 and poured into a flame dried 1 L 1 neck rbf equipped with a magnetic stir bar and sealed with a rubber septum. A Drierite drying tube was attached and the solution cooled to -30 °C (on further cooling CCl_4 freezes). Cloudiness or precipitate is indicative of moisture. N_2O_5 (26.6 g 0.25 mol; freshly sublimed into a tared 500 mL rbf) is dissolved in CCl_4. This is best done by venting the N_2O_5 to Ar, removing the vacuum line adapter, quickly adding 300 mL CCl_4 and sealing the solution with a rubber septum. N_2O_5 will dissolve on swirling. This solution is kept at -30 °C during the addition. An oven dried 18 gauge cannula connects the two solutions. Pressurizing the N_2O_5 solution with an Ar balloon initiates the addition. The rate of addition should be such that a continuous stream is nearly reached. The addition requires 2 h, then the mixture is slowly allowed to warm to rt and stir overnight. The solvent is removed on a rotary evaporator with a water bath temperature of 35 °C. A thin film IR of the yellow oil shows strong bands at 2140 (N_2), 1740 (C=O), 1650 (ONO_2), 1560 (NO_2) cm^{-1}. If no diazo band is present, the reaction has failed. TLC (15% Et_2O/pet ether) shows two major spots, the nitrate ester runs faster than the product. Pure ENDA is obtained by chromatography. Thus the above reaction mixture is loaded onto an 8 cm x 22 cm silica gel column and eluted with solvent (1 L 0%, 1 L 5%, 1 L 10 %, 1 L 15 %, 1 L 20 %, 1 L 30 % ether/pet ether). The nitrate ester elutes first, and the product follows as a yellow band. Fractions are collected in 500 mL Erlenmeyer flasks. The yellow fractions are analysed for presence of nitrate ester by TLC. Concentration of the appropriate fractions affords 29 g (0.18 mol, 73 %) pure product. This material is stored at 5 °C until use. ^{13}C NMR: δ 13.8, 62.7, 101.3 (C-N_2), 154.9

***tert*-Butyl Nitrodiazoacetate (TBNDA) (8).** *Tert*-butyl diazoacetate (TBDA) was prepared exactly as described in Organic Syntheses.[38] An alternative procedure may also be scaled up with ease.[38b] Thus tert-butyl acetoacetate (63.2 g, 0.40 mol) and toluenesulfonyl azide (79.2 g, 0.4 mol) are dissolved in 1.2 L pentane along with 2.6 g tetrabutylammonium bromide. A cold solution of NaOH (32 g, 0.8 mol in 260 mL water) is slowly added to the organic solution. This biphasic mixture is stirred at rt for 2 days. The organic layer is separated, and the aqueous is extracted 1 x with 200 mL pentane. The combined organic layers are washed 1 x with 500 mL water and 1 x with 500 mL brine and dried with magnesium sulfate. Concentration on a rotary evaporator followed by vacuum distillation[38a] affords 41.6 g (0.29 mol, 73 %) TBDA. The nitration is conducted exactly as is described for EDA. Thus from 31 g (0.22 mol) TBDA and 11.8 g (0.11 mol) N_2O_5 a yellow oil is obtained that is chromatographed (5 cm x 25 cm silica colum, 1.5 L 0 %, 1 L 2 %, 1 L 7 %, 1 L 15 % ether/pet ether) to yield 15.8 g (85 mmol, 77%) TBNDA. Pure TBNDA crystallizes on standing at 5 °C and melts at 31-33 °C.

Cyanonitrodiazomethane (6). A solution of dinitrogen pentoxide (3.5g, 33 mmol) in methylene chloride at -78 °C was added dropwise over 1 h to 120 ml of a 0.5M solution of diazoacetonitrile[39] in methylene chloride at -78 °C.. After the addition was complete the mixture was warmed to rt over ca. 3 h. An insoluble precipitate was filtered off and the crude solution was concentrated to 15 mL and stored at 5 °C until use. IR 2240, 2160, 1670, 1530 cm^{-1}.

Nitrodiazoacetophenone (9).[8] Diazoacetophenone[40] (4.1 g, 27.9 mmol) was dissolved in 50 mL CH_2Cl_2. This solution was dried with magnesium sulfate and filtered through a fritted funnel into a flame dried 250 mL 1 neck rbf equipped with a magnetic stirring bar. A drying tube was attached and the solution cooled to -78 °C. N_2O_5 (1.5 g, 13.9 mmol in 40 mL CH_2Cl_2) was added over 1 h. The reaction mixture was warmed to rt over 4 h and then concentrated to 15 mL on a rotary evaporator. After storing overnight in a freezer, 1.42 g (7.4 mmol, 51 %) of crystalline product was collected.

Toluenesulfonylnitrodiazomethane (10). Due to the sensitivy of both the starting material and the product, exposure to light was minimized during the following procedure: Toluenesulfonyldiazomethane[41] (3.0 g, 15.5 mmol) was dissolved in 50 mL CH_2Cl_2. This solution was dried with sodium sulfate and filtered through a fritted funnel into a flame dried 100 mL 1 neck rbf equipped with a magnetic stirring bar. A drying tube was attached and the solution cooled to -78 °C. A solution of N_2O_5 (0.86 g, 7.9 mmol in 20 mL CH_2Cl_2) was added over 1 h. The reaction mixture was warmed to rt over 4 h and then concentrated to 10 mL on a rotary evaporator. After storing overnight in a freezer, 880 mg (3.7 mmol, 47 %) of crystalline product was collected. This material was very light and temperature sensitve, giving off copious amounts of gas after very short periods of time at rt. ^1H NMR: δ 2.41 (s, 3 H), 7.33 (d, J = 7.1 Hz, 2 H), 7.87 (d, J = 7.1 Hz, 2 H). ^{13}C NMR: δ 21.7, 110 (C-N_2), 128.8, 130.1, 135.8, 147.0. IR 2140, 1525, 1360, 1220 cm^{-1}. Mp 64 °C, dec.

Trifluoromethylnitrodiazomethane (11). N_2O_5 (4.7 g, 44 mmol in 50 mL CH_2Cl_2) is added to 150 mL of a 0.58 M solution (determined by measuring the amount of gas evolved from an aliquot of solution when mixed with 10% HCl) of trifluoromethyldiazomethane[42] in CH_2Cl_2 at -78 °C via a cannula over 40 min. The mixture was warmed to 0 °C over 3 h and carefully concentrated on a rotary evaporator with the water bath at 5 °C. The nitrate ester side product distills off and care must be taken that the volatile product is not lost. Approx 1.5 g (11 mmol, 25 %) pure product is obtained. IR (gas phase) 2110, 1550, 1260 cm^{-1}. This material has a half life of about 2 h at rt. In methylene chloride solution it may be stored for 1-2 weeks at 5 °C.

Nitrodiazoacetic acid (12).[9] A face shield and heavy gloves should be worn during the following procedure. For every 100 mg TBNDA (8) 50-100 μL neat trifluoroacetic acid (TFA) is added. This procedure has been used for amounts ranging from 100 mg to 2.0 g TBNDA. **Nitrodiazoacetic acid is highly explosive** and attention must be paid during the entire procedure. Of particular importance is never to have any nitrodiazoacetic acid around for more than 30-45 min. ***It should be used as soon as it is made.*** Thus crystalline TBNDA (1.0 g, 5.3 mmol) is placed in a 10 mL pear flask equipped with magnetic stirring bar. TFA (0.5 mL) is added and the mixture is stirred efficiently. After 2-15 min, the yellow solution will turn into a white solid, at this point excess TFA is pipetted off and nitrodiazoacetic acid is washed 2 x with 1 mL hexane. Mp 53 °C (dec), IR 2160, 1755, 1515, 1320 cm^{-1}. If the deprotection mixture does not solidify within 15 minutes, excess TFA can be removed on a rotary evaporator behind a blast shield, and the mixture should solidify. If formation of nitrodiazoacetic acid is not observed after 15 min of concentrating, the rxn mixture should be discarded.

Nitrodiazomethane (13). A face shield and heavy gloves should be worn during the following procedure. Nitrodiazoacetic acid (12) is prepared by deprotection of 1 g tert-butyl nitrodiazoacetate (8). It is washed with hexane in a 10 mL pear flask. Methylene chloride (6 mL) is added and the heterogeneous mixture is stirred. Water (1.5 mL) is added dropwise to this mixture. The acid dissolves in the water and decarboxylation commences as indicated by the presence of a green color in both layers. After several minutes of stirring, the organic layer containing nitrodiazomethane is pipetted off, 2 mL fresh CH_2Cl_2 is added and the aqueous layer is extracted. This process is repeated 2 x or until no color remains in the aqueous layer. The 10 mL of organic material may then be safely concentrated to 2 mL by blowing air over the top of the solution. Nitrodiazomethane can be safely handled in methylene chloride solution, it is, however, **extremely explosive as a neat liquid**. IR 3110, 2110, 1490, 1320 cm^{-1}. ^{13}C NMR: δ 89.6; J_{CH} = 240 Hz.

Rhodium(II) Cyclopropanation of Alkenes with Nitrodiazo Compounds

Catalytic Cyclopropanation using Ethyl Nitrodiazoacetate (7). ENDA (7) (1 - 10 mmol) was added dropwise via a pasteur pipet to a stirred mixture of alkene (5 - 50 equivalents) and rhodium(II) acetate (3 mol %) under ambient conditions such that nitrogen evolution was not too vigorous. After completion of addition, the mixture was stirred for 30 minutes. Excess alkene was evaporated and the ene and cyclopropane products were separated by flash column chromatography (0 - 50% ether/hexane). In most cases the major isomer could be separated from the minor by selective saponification. The spectra of compounds **43-51** and **69** and **70** have been reported in reference 3b.

Large scale cyclopropanation with ENDA (7). One half of the crude nitration mixture obtained from the reaction between 14.4 g (0.13 mol) N_2O_5 and 30.3 g (0.26 mol) ethyl diazoacetate was diluted with 10 mL CH_2Cl_2 and added dropwise over 1 h from a jacketed addition funnel cooled with ice water to 15 g (0.13 mol) styrene and 100 mg (0.25 mmol) rhodium(II) acetate in 5 mL methylene chloride at 5 °C. After 2 h no more nitrogen evolution was observed, the mixture was stirred for an additional hour and then concentrated and filtered through flash silica (5 cm x 5 cm) eluting first with pentane to remove excess styrene and then with 20 % ether in hexane to afford, after concentration, 21 g (0.11 mol, 85 %) of nitrocyclopropane carboxylates **43** and **44.**

Catalytic Cyclopropanation of Alkenes with Nitrodiazomethane (13). A solution of nitrodiazomethane in methylene chloride was titrated with sulfuric acid. Aliquats of this solution were added to alkenes and catalyst cooled in an ice bath as described for

ENDA. In nearly all cases the product nitrocyclopropanes could be separated by column chromatography. They are volatile and care must be taken when concentrating column fractions.

***trans*-(2-Nitrocyclopropyl)benzene (23).**[2a,31] ^{1}H NMR: δ 1.62 (m, 1 H), 2.18 (m, 1 H), 3.06 (m, 1 H), 4.33 (m, 1 H), 7.13 (m, 5 H)

***cis*-(2-Nitrocyclopropyl)benzene (24).**[31] ^{1}H NMR: δ 1.58 (m, 1 H), 2.30 (m, 1 H), 2.80 (m, 1H), 4.57 (m, 1 H), 7.16-7.23 (m, 5 H). ^{13}C NMR: δ 13.5, 28.5, 61.6, 128.0, 128.4, 129.2, 132.4. IR 1540, 1360 cm^{-1}.

1,1-Dimethyl-2-nitrocyclopropane (25).[5a,31] ^{1}H NMR: δ 1.10 (t, J = 6.5 Hz, 1 H), 1.15 (s, 3 H), 1.23 (s, 3 H), 1.72 (dd, J = 4.2, 6.0 Hz, 1 H), 4.02 (dd, J = 4.2, 6.8 Hz, 1 H).

2-n-Butylnitrocyclopropane (ca. 1.4:1 trans/cis mixture of inseparable isomers) (26, 27). ^{1}H NMR: δ 0.7-1.8 (m, 12 H), 3.95 (m, .55 H), 4.30 (m, .45 H). IR 1550, 1370 cm^{-1}. HRMS (M+H) 144.1001, calcd for $C_7H_{14}NO_2$ 144.1024.

***trans,trans*-1,2-Dimethyl-3-nitrocyclopropane (28).**[31] ^{1}H NMR: δ 1.08 (m, 6 H), 2.06 (m, 2 H), 3.63 (t, J = 3.2 Hz, 1 H). ^{13}C NMR: δ 10.2, 24.7, 66.8. IR 1540, 1360 cm^{-1}. HR-MS (M+NH$_4^+$) 133.096, calcd for $C_5H_{13}N_2O_2$ 133.097.

***cis,cis*-1,2-Dimethyl-3-nitrocyclopropane (29).** ^{1}H NMR: δ 1.22 (m, 6 H), 1.60 (m, 2 H), 4.18, (t, J = 8.0 Hz, 1 H).

***anti*-7-Nitrobicylo[4.1.0]heptane (30).**[31] ^{1}H NMR: δ 1.11 (m, 2 H), 1.30 (m, 2 H), 1.74 (m, 2 H), 1.92 (m, 2 H), 2.20 (m, 2 H), 4.03 (t, J = 3.0 Hz, 1 H). ^{13}C NMR: δ 18.7, 20.4, 21.5, 64.7. IR 1540, 1360 cm^{-1}. HR-MS (M+H$^+$) 142.088, calcd for $C_7H_{12}NO_2$ 142.087.

***syn*-7-Nitrobicyclo[4.1.0]heptane (31).** ^{1}H NMR: δ 1.27 - 1.44 (m, 4 H) 1.54 - 1.64 (m, 4 H), 1.96 (m, 2 H), 4.06 (t, J = 8.0 Hz, 1 H).

3-Nitro-1,1,2,2-tetramethylcyclopropane (32).[3a] ^{1}H NMR: δ 1.20 (s, 6 H), 1.34 (s, 6 H), 3.77 (s, 1 H), ^{13}C NMR: δ 16.0, 22.3, 32.8, 74.3. IR 1535, 1360, 1110 cm^{-1}. Mp 48 - 49°C. HRMS (M+H$^+$) 144.102, calcd for $C_7H_{14}NO_2$ 144.103.

***cis,trans*-1,2-Dimethyl-3-nitrocyclopropane (33).** ^{1}H NMR: δ 1.07 (d, J = 6.2 Hz, 3 H), 1.20 (d, J = 5.7 Hz, 3 H), 1.30 (m, 1 H), 1.85 (m, 1 H), 3.96 (dd, J = 3.5, 7.9 Hz, 1 H). ^{13}C NMR δ 10.7, 16.1, 25.3, 27.9, 66.1. IR 1540, 1360 cm^{-1}.

***trans*-(2-Nitrocyclopropyl) acetate (67).** ^{1}H NMR: δ 1.65 (m, 1 H), 2.06 (s, 3 H), 2.14 (m, 1 H), 4.39 (m, 1 H), 4.82 (m, 1 H). IR 1760, 1550, 1370 cm^{-1}. HRMS (M+H) 146.0471, calcd for $C_5H_8NO_4$ 146.0453.

***cis*-(2-Nitrocyclopropyl) acetate (68).** ^{1}H NMR: δ 1.59 (m, 1 H), 2.06 (s, 3 H), 2.26 (m, 1 H), 4.32 (m, 1 H), 4.44 (m, 1 H).

Catalytic Cyclopropanation of Alkenes with Nitrocyanodiazomethane (6). The crude solution obtained from the nitration was used to cyclopropanate the olefins. This crude solution was added to a stirred solution of catalyst and neat alkene cooled in an ice bath. After stirring the reaction mixture for 30 min, ether (5 mL) and a saturated solution of sodium carbonate (25 ml) is added. Stirring is continued for an additional hour. More ether is added, the layers are separated, the organic layer is washed 3 x with water and once with brine then dried and concentrated to yield pure nitrocyclopropanecarbonitriles. A band in the IR at 1670 cm^{-1} or an absorption in the ^{1}H NMR spectrum at 5.3 ppm is due to the nitrate side product ($NCCH_2ONO_2$). This material can be removed by stirring with saturated sodium carbonate. Compound **34** could be separated from **35** by fcc. The other isomeric mixtures could not be separated.

***cis*-1-Nitro-2-phenylcyclopropanecarbonitrile (34).** ^{1}H NMR: δ 2.36 (dd, J = 6.9, 10.3 Hz, 1 H), 2.72 (dd, J = 6.9, 10.3 Hz, 1 H), 3.67 (t, J = 10.3 Hz, 1 H), 7.22 (m, 2 H), 7.36 (m, 3 H). ^{13}C NMR: δ 24.7, 38.2, 60.6, 111.2, 128.2, 129.2, 129.6, 130.5. IR 2250, 1560, 1350 cm^{-1}. HRMS (M+NH$_4$) 206.093, calcd for $C_{10}H_{12}N_3O_2$ 206.093. Mp 104 - 105 °C.

***trans*-1-Nitro-2-phenylcyclopropanecarbonitrile (35).** ^{1}H NMR: δ 2.30 (dd, J = 7.3, 10.3 Hz, 1 H), 2.90 (dd, J = 7.3, 10.3 Hz, 1 H), 3.52 (t, J = 10.3 Hz, 1 H), 7.22-7.36 (m, 5 H).

2,2-Dimethyl-1-nitrocyclopropanecarbonitrile (36). ^{1}H NMR: δ 1.32 (s, 3 H), 1.45 (s, 3 H), 1.73 (d, J = 7.0 Hz, 1 H) 2.37 (d, J = 7.0 Hz, 1 H). IR 2260, 1560, 1340 cm-1. HRMS (M+NH$_4$) 158.092, calcd for $C_6H_{12}N_3O_2$ 158.093. Mp 64 - 65 °C.

2-Butyl-1-nitrocyclopropanecarbonitrile (3:1 cis/trans mixture of isomers)(37, 38). ^{1}H NMR: δ .92 (m, 3 H), 1.22 - 1.60 (m, 7 H), 1.98 (m, 0.25 H), 2.21 (m, 0.75 H), 2.40 (m, 1 H). ^{13}C NMR: δ 13.7, 13.8, 22.0, 24.5, 25.6, 27.6, 29.6, 30.1, 30.2, 34.5, 36.1, 57.4, 59.0, 112.1, 114.2. IR 2260, 1560, 1360 cm^{-1}. HRMS (M+NH$_4$) 186.127, calcd for $C_8H_{16}N_3O_2$ 186.125.

***cis,cis*-2,3-Dimethyl-1-nitrocyclopropanecarbonitrile (39).** ^{1}H NMR: δ 1.28 (m, 6 H), 2.62 (m, 2 H). ^{13}C NMR: δ 8.9, 33.4, 65.0, 110.8. IR 2260, 1560, 1340 cm^{-1}. IR 2260, 1560, 1340 cm^{-1}. HRMS (M+NH$_4$) 158.092, calcd for $C_6H_{12}N_3O_2$ 158.093. Mp 62 - 65°C.

***syn*-7-Nitrobicyclo[4.1.0]heptane-7-carbonitrile (40).** ^{1}H NMR: δ 1.29-1.58 (m, 4 H), 1.85 (m, 2 H), 2.11 (m, 2 H), 2.70 (m, 2 H). ^{13}C NMR: δ 19.4, 19.5, 33.1, 64.3, 111.6. HRMS (M+NH$_4$) 184.109, calcd for $C_8H_{14}N_3O_2$ 184.108. Mp 68 - 70 °C.

1-Nitro-2,2,3,3-tetramethylcyclopropanecarbonitrile (41).[21] ^{1}H NMR: δ 1.39 (s, 6 H). 1.40 (s, 6 H). ^{13}C NMR: δ 17.0, 20.9, 40.3, 71.5, 113.1. IR 2245, 1555, 1340 cm^{-1}. HRMS (M+NH$_4$) 186.121, calcd for $C_8H_{16}N_3O_2$ 186.124. Mp 68 - 69 °C.

***cis,trans*-2,3-Dimethyl-1-nitrocyclopropanecarbonitrile (42).** ^{1}H NMR: δ 1.35 (t, J = 6.5 Hz, 6 H), 1.92 (m, 1 H), 2.60 (m, 1 H). ^{13}C NMR: δ 10.9, 14.8, 32.9, 38.5, 64.3, 112.8. IR 2260, 1560, 1340 cm^{-1}.

Catalytic Cyclopropanation of Alkenes with t-Butyl nitrodiazoacetate (8). The procedure was the same as given for ENDA (7). Compounds **52** and **53** could be separated by chromatography. The other isomeric cyclopropyl esters could not be separated by either chromatography or saponification.

(1,1-Dimethylethyl) *cis*-1-nitro-2-phenylcyclopropanecarboxylate (52). ^{1}H NMR: δ 1.07 (s, 9 H), 2.06 (dd, J = 6.5 Hz, 10.6 Hz, 1 H), 2.32 (dd, J = 6.5, 9.0 Hz, 1 H), 3.67 (t, J = 9.6 Hz, 1 H), 7.24 (m, 5 H). ^{13}C NMR: δ 21.2, 27.3, 33.6, 72.4, 83.7, 128.1, 128.4, 128.7, 132.3, 160.6. IR 1740, 1540, 1350 cm^{-1}. HRMS (M+H) 263.127, calcd for $C_{14}H_{18}NO_4$ 264.124. Anal. calcd for $C_{14}H_{17}NO_4$ C, 63.87; H, 6.51. Found: C, 63.78; H, 6.58. Mp 89 - 90 °C.

(1,1-Dimethylethyl) *trans*-1-nitro-2-phenylcyclopropanecarboxylate (53). ^{1}H NMR: δ 1.48 (s, 9 H), 1.88 (dd, J = 6.6, 10.0 Hz, 1 H), 2.55 (dd, J = 6.6, 9.8 Hz, 1 H), 3.66 (dd, J = 9.2, 10.0, 1 H), 7.24 (m, 5 H). ^{13}C NMR: δ 19.5, 27.8, 32.9, 73.3, 84.6, 128.3, 128.4, 128.5, 131.8, 164.0.

(1,1-Dimethylethyl) 2,2-dimethyl-1-nitrocyclopropanecarboxylate (54). ^{1}H NMR: δ 1.17 (s, 3 H), 1.29 (s, 3 H), 1.42 (s, 9 H), 1.59 (d, J = 6.6 Hz, 1 H), 1.74 (d, J = 6.6 Hz, 1 H). IR 1730, 1545, 1350 cm^{-1}. HRMS (M+NH_4) 233.149, calcd for $C_9H_{21}N_2O_4$ 233.150.

(1,1-Dimethylethyl) *cis,cis*-2,3-dimethylnitrocyclopropanecarboxylate (55). ^{1}H NMR: δ 1.11 (m, 6 H), 1.43 (s, 9 H), 2.17 (m, 2 H). IR 1740, 1540, 1350 cm^{-1}. HRMS (M+NH_4) 233.151, calcd for $C_9H_{21}N_2O_4$ 233.150.

(1,1-Dimethylethyl) *syn*-7-nitrobicyclo[4.1.0]heptane-7-carboxylate (56). ^{1}H NMR: δ 1.08 (m, 2 H), 1.21 (m, 2 H), 1.48 (s, 9 H), 1.90 (m, 4 H), 2.22 (m, 2 H). IR 1740, 1540, 1350 cm^{-1}. HRMS (M+NH_4) 259.164, calcd for $C_{12}H_{23}N_2O_4$ 259.166.

Catalytic Cyclopropanation of Alkenes with Nitrodiazoacetopheneone (9). The procedure was the same as given for ENDA (7). Compound **57** was purified by fractional crystallization. The other isomeric products were not separable.

(*trans*-1-Nitro-2-phenylcyclopropyl)phenyl methanone (57). ^{1}H NMR: δ 1.92 (dd, J = 6.6, 9.8 Hz, 1 H), 2.97 (dd, J = 6.6, 9.8 Hz, 1 H), 3.81 (t, J = 9.8 Hz, 1 H), 7.28 (s, 5 H), 7.43 (m, 2 H), 7.54 (m, 1 H), 7.84 (m, 2 H). ^{13}C NMR: δ 21.3, 32.3, 76.8, 128.0, 128.4, 128.6, 128.7, 128.9, 129.0, 131.0, 133.9, 134.9, 188.6. IR 1695, 1530, 1350 cm^{-1}. Mp 134 - 135 °C. HRMS (M+H) 268.098, calcd for $C_{16}H_{14}NO_3$ 268.100. Anal. calcd for $C_{16}H_{14}NO_3$: C, 71.90; H, 5.28. Found: C, 71.36; H, 4.95. Mp 134 - 135 °C. The minor isomer exhibited peaks in the ^{1}H NMR spectrum: δ 2.21 (dd, 1 H), 2.67 (dd, 1 H), 4.02 (t, 1 H).

(2,2-Dimethyl-1-nitrocyclopropyl)phenyl methanone (58). ^{1}H NMR: δ 1.05 (s, 3 H), 1.55 (s, 3 H), 1.78 (d, J = 6.3, 1 H), 2.10 (d, J = 6.1 Hz, 1 H), 7.39-7.45 (m, 2 H), 7.55 (m, 1 H), 7.82 (m, 2 H). IR 1690, 1540, 1340 cm^{-1}. HRMS (M+H) 220.102, calcd for $C_{12}H_{14}NO_3$ 220.099.

(*trans,trans*-2,3-Dimethyl-1-nitrocyclopropyl)phenyl methanone (59). ^{1}H NMR: δ 1.35 (m, 6 H), 2.15 (m, 2 H), 7.4 - 7.8 (m, 5 H). IR 1695, 1600, 1540, 1360 cm^{-1}. HRMS (M+H) 220.096, calcd for $C_{12}H_{14}NO_3$ 220.099.

(*cis,cis*-2,3-Dimethyl-1-nitrocyclopropyl)phenyl methanone (60). ^{1}H NMR: δ 1.11 (m, 6 H), 2.52 (m, 2 H), 7.4-7.8 (m, 5 H).

(*anti*-7-Nitrobicyclo[4.1.0]hept-7-yl)phenyl methanone (61). ^{1}H NMR: δ 1.26 (m, 2 H), 1.36 (m, 2 H), 1.77 (m, 2 H), 2.07 (m, 2 H), 2.22 (m, 2 H), 7.40 (m, 2 H), 7.51 (m, 1 H), 7.72 (m, 2 H). ^{13}C NMR: δ 18.6, 20.2, 27.8, 79.6, 127.7, 128.7, 133.2, 135.5, 191.4. IR 1695, 1600, 1540, 1360 cm^{-1}. HRMS (M+H) 246.109, calcd for $C_{14}H_{16}NO_3$ 246.112.

Catalytic Cyclopropanation of Alkenes with Toluenesulfonylnitrodiazomethane (10). The procedure was the same as that given for ENDA (7). The isomeric products were not separable.

(*cis*-1-Nitro-2-phenylcyclopropyl)sulfonyl-4-methylbenzene (62). ^{1}H NMR: δ 2.47 (s, 3 H), 2.61 (dd, J = 7.2, 10.6 Hz, 1 H), 2.85 (dd, J = 7.2, 9.6 Hz, 1 H), 3.64 (t, J = 10.1, 1 H), 7.02 - 7.48 (m, 7 H), 7.96 (d, J = 8.4 Hz, 2 H). IR 1600, 1550, 1350 cm^{-1}. HRMS (M+NH_4) 335.104, calcd for $C_{16}H_{19}N_2O_4S$ 335.107.

(*trans*-1-Nitro-2-phenylcyclopropyl)sulfonyl-4-methylbenzene (63). ^{1}H NMR: δ 2.37 (s, 3 H), 2.71 (dd, J = 7.1, 10.9 Hz, 1 H), 3.02 (dd, J = 7.1, 10.3 Hz, 1 H), 3.49 (t, J = 10.6, 1 H), 7.02 - 7.48 (m, 7 H), 7.79 (d, J = 8.3 Hz, 2 H).

(2,2-Dimethyl-1-nitrocyclopropyl)sulfonyl-4-methylbenzene (64). ^{1}H NMR: δ 1.08 (s, 3 H), 1.54 (s, 3 H), 2.12 (d, J = 7.5 Hz, 1 H), 2.16 (d, J = 7.5 Hz, 1 H), 2.40 (s, 3 H), 7.30 (d, J = 8.3 Hz, 2 H), 7.76 (d, J = 8.3 Hz, 2 H). ^{13}C NMR: δ 19.7, 21.8, 26.3, 32.3, 90.3, 129.6, 129.7, 134.6, 146.0. IR 1595, 1550 cm^{-1}. HRMS (M+NH_4) 287.108, calcd for $C_{12}H_{19}N_2O_4S$ 287.107.

(*cis,cis*-2,3-Dimethyl-1-nitrocyclopropyl)sulfonyl-4-methylbenzene (65). ^{1}H NMR: δ 1.60 (m, 6 H), 2.38 (s, 3 H), 2.63 (m, 2 H), 7.26 (d, J = 8.6 Hz, 2 H), 7.83 (d, J = 8.6 Hz, 2 H). IR 1595, 1550 cm^{-1}. HRMS (M+NH_4) 287.105, calcd for $C_{12}H_{19}N_2O_4S$ 287.107. Absorptions at 1.1 ppm in the ^{1}H NMR spectrum were assigned to the methyl groups of the minor isomer **84**.

(*syn*-7-Nitrobicyclo[4.1.0]hept-7-yl)sulfonyl-4-methylbenzene (66). ^{1}H NMR: δ 1.35, (m, 2 H), 1.72 (m, 2 H), 1.55 - 2.36 (m, 4 H), 2.39 (s, 3 H), 2.61 (m, 2 H), 7.29 (d, J = 8.4 Hz, 2 H), 7.84 (d, J = 8.4 Hz, 2 H). IR 1595, 1550, 1340 cm^{-1}. HRMS (M+NH_4) 313.124, calcd for $C_{14}H_{21}N_2O_4S$ 313.122.

Catalytic Cyclopropanation of Alkenes with Trifluoromethylnitrodiazomethane (11). The procedure was the same as given for ENDA (7). Compound **71** could be separated from **72** by fractional crystallization. Other isomeric nitrocyclopropanes could not be separated and in general were not stable for more than one or two days. The cyclopropanes are volatile and care must be excercised when concentrating column fractions. No stereochemical assignments were made.

[2-Nitro-2-(trifluoromethyl)cyclopropyl]benzene (71) Isomer A. ^{1}H NMR: δ 2.25 (dd, J = 6.8, 9.5 Hz, 1 H), 2.59 (dd, J = 6.8, 10.5 Hz, 1 H), 3.60 (t, J = 10.0 Hz, 1 H), 7.25 - 7.39 (m, 5 H). ^{13}C NMR: δ 18.5, 35.2, 128.7, 129.1, 130.7. IR 1560, 1350, 1180 cm^{-1}. HRMS (M+H) 232.056, calcd for $C_{10}H_9F_3NO_2$ 232.059. Mp 71 - 73 °C.

[2-Nitro-2-(trifluoromethyl)cyclopropyl]benzene (72) Isomer B. ^{1}H NMR: δ 2.12 (dd, J = 7.3, 10.5 Hz, 1 H), 2.70 (dd, J = 7.3, 9.5 Hz, 1 H), 3.19 (t, J = 10 Hz, 1 H), 7.25 - 7.39 (m, 5 H). ^{13}C NMR: δ 17.0, 31.6, 128.8, 128.9, 129.9.

1,1-Dimethyl-2-nitro-2-(trifluoromethyl)cyclopropane (73). ^{1}H NMR: δ 1.49 (s, 6 H), 3.04 (q, J = 2.0 Hz, 2 H). HRMS (M+NH_4) 201.082, calcd for $C_6H_{12}F_3N_2O_2$ 201.085.

2-Nitro-2-(trifluoromethyl)cyclopropyl acetate (74) Isomer A. ^{1}H NMR: δ 2.05 (s, 3 H), 2.16 (dd, J = 6.3, 8.7 Hz, 1 H), 2.64 (m, 1 H), 4.59 (dd, J = 6.6, 8.1 Hz, 1 H). IR 1760, 1560, 1360 cm^{-1}. HRMS (M+NH_4) 231.060, calcd for $C_{10}H_6F_3N_2O_4$ 231.059.

2-Nitro-2-(trifluoromethyl)cyclopropyl acetate (75) Isomer B. ^{1}H NMR: δ 2.01 (s, 3 H), 2.10 (m, 1 H), 2.61 (m, 1 H), 4.93 (m, 1 H).

Methyl *trans*-1-nitro-2-phenylcyclopropanecarboxylate (77). Methyl nitrodiazoacetate (**76**)[8,9] (prepared by treatment of nitrodiazoacetic acid with diazomethane)[9] was added to styrene containing a few mg catalyst. Chromatography over silica gel afforded the pure product: ^{1}H NMR: δ 2.12 (dd, J = 6.5, 10.6 Hz, 1 H), 2.44 (dd, J = 6.5, 9.0 Hz, 1 H), 3.43 (s, 3 H), 3.76 (t, J = 9.6 Hz, 1 H), 7.13-7.33 (m, 5 H). IR 1740, 1540, 1350 cm^{-1}. HRMS (M+NH_4) 239.1049, calcd for $C_{11}H_{15}N_2O_4$ 239.1031.

Ethyl *syn*-3-nitro-*exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene-3-carboxylate (93). ENDA (7) was added dropwise to excess norbornadiene. After standard workup and chromatography **93** was obtained in 20 % yield and contaminated with 5 - 10% of a minor isomer. ^{1}H NMR: δ .88 (d, J = 11.0 Hz, 1 H), 1.08 (d, J = 11.0 Hz, 1 H), 1.26 (t, J = 7.1 Hz, 3 H), 2.29 (s, 2 H), 3.2 (br, 2 H), 4.24 (q, J = 7.1 Hz, 2 H), 6.47 (t, J = 1.5 Hz, 2 H). IR 1750, 1550 cm^{-1}.

Ring Opening Reactions of Ethyl Nitrocyclopropanecarboxylates. For the most part the literature procedure[27] was followed.

Ethyl 4-cyano-2-nitro-4-phenylbutanoate (1:1 mixture of diastereomers) (94). Trans phenyl ester **43** (110 mg, 0.47 mmol) was heated for three h at 60 °C in 1 mL DMF containing excess sodium cyanide. After cooling, several drops of a saturated ammonium chloride solution were added, the mixture acidified to pH = 4 with acetic acid, extraction with ether followed by washing with water and drying afforded 50 mg (0.19 mmol, 41 %) of a diasteromeric mixture of products. ^{1}H NMR: δ 1.24 (m, 3 H), 2.57 - 2.94 (m, 2 H), 3.84 -2.91 (m, 1 H), 4.18 - 4.28 (m, 2 H), 4.94 - 4.99 (m, .5 H), 5.28 (m, .5 H), 7.25 -7.42 (m, 5 H). ^{13}C NMR: δ 13.7, 33.7, 34.1, 35.4, 35.9, 63.7, 84.4, 85.1, 118.6, 118.9, 127.2, 127.4, 128.4, 129.0, 129.2, 129.5, 129.7, 132.8, 133.3, 163.2, 163.3. IR 2240, 1750, 1560 cm^{-1}. HRMS (M+H) 263.108, calcd for $C_{13}H_{15}N_2O_4$ 263.104.

Ethyl 2-nitro-4-phenyl-4-phenylaminobutanoate (1:1 mixture of diastereomers) (95). Trans phenyl ester **43** (110 mg, 0.47 mmol) was heated at reflux for 15 h in methanol containing 300 µL aniline. The mixture was cooled, concentrated first on a rotary evaporatior and then on a vacuum line and chromatographed (0 -10 % ether/hexane) to afford 145 mg (0.44 mol, 95 %) of a 1:1 isomeric mixture of inseparable diasteromers. ^{1}H NMR: δ 1.22 (m, 3 H), 2.52 -2.58 (m, 1H), 2.71 - 2.81 (m, 1 H), 3.55 (br, 0.5 H), 4.18 (br, 0.5 H), 4.24 (m, 2 H), 4.46 (br, 1 H), 5.03 (m, 0.5 H), 5.38 (m, 0.5 H), 6.52 (m, 2 H), 6.68 (m, 2 H), 7.14 (m, 2 H), 7.22 -7.33 (m, 4 H). ^{13}C NMR: δ 13, 37.9, 38.4, 54.5, 55.1, 63.2, 85.6, 86.6, 113.7, 113.9, 115.0, 118.3, 118.4, 118.5, 126.0, 126.2, 126.7, 128.0, 128.9, 129.0, 129.1, 140.9, 141.3, 146.3, 146.4, 164.3, 164.7. IR 3380 (br), 1750, 1600, 1560, 1500 cm^{-1}. HRMS (M+H) 329.147, calcd for $C_{18}H_{21}N_2O_4$ 329.150.

Ethyl 4-methyl-4-methoxy-2-nitropentanoate (96). Gem dimethyl ester **45** (60 mg, 0.33 mmol) was heated at reflux in methanol for 48 h. Concentration of the reaction mixture on a rotary evaporator afforded 70 mg (0.32 mmol, 96 %) product. ^{1}H NMR: δ 1.11 (s, 3 H), 1.55 (s, 3 H), 1.24 (t, J = 7.2 Hz, 3 H), 2.30 (dd, J = 4.2, 15.4 Hz, 1 H), 2.52 (dd, J = 8.0, 15.4 Hz, 1 H), 3.07 (s, 3 H), 4.20 (q, J = 7.2 Hz, 2 H), 5.28 (dd, J = 4.2, 8.0 Hz, 1 H). ^{13}C NMR: δ 13.9, 24.2, 24.7, 40.5, 49.4, 63.0, 72.9, 84.8, 165.3. IR 1750, 1560, 1370 cm^{-1}. HRMS (M+H) 220.122, calcd for $C_9H_{18}NO_5$ 220.119.

Ethyl 2,4-dibromo-4-methyl-2-nitropentanoate (97). Gem dimethyl ester **45** (40 mg, 0.22 mmol) was dissolved in 1 mL CCl_4. A few drops of bromine were added and the mixture was warmed to 50 °C and stirred for 2 h. After fcc 28 mg (0.08 mmol, 36 %) product was obtained along with 22 mg (55 %) isoxazoline N-oxide **100**. ^{1}H NMR: δ 1.26 (t, J = 7.1 Hz, 3 H), 1.82 (s, 3 H), 1.88 (s, 3 H), 3.27 (d, J = 16.4 Hz, 1 H), 3.44 (d, J = 16.4 Hz, 1 H), 4.28 (q, J = 7.1 Hz, 2 H). ^{13}C NMR: 13.5, 34.6, 34.7, 52.2, 59.6, 64.8, 91.2, 162.8. IR 1750, 1570 cm^{-1}.

Ethyl 2,4-dibromo-2-nitro-4-phenylbutanoate (1:1 mixture of diastereomers) (98). Trans phenyl ester **43** (15 mg, 0.06 mmol) was stirred in 0.5 mL CCl_4. Three drops of bromine were added. The solution was warmed to 50 °C and stirred for 1 h. After concentrating the reaction mixture 24 mg (0.06 mmol, 100 %) of diasteromeric dibromides were obtained. ^{1}H NMR δ 1.14 - 1.27 (m, 3 H), 3.36 -3.71 (m, 2 H), 4.01 - 4.08 (m, 1H), 4.23 (m, 1 H), 5.14 - 5.20 (m, 0.5 H), 5.22 - 5.28 (m, 0.5 H), 7.22 - 7.38 (m, 5 H). ^{13}C NMR: d 13.4, 13.5, 47.2, 47.4, 47.5, 64.7, 64.8, 92.6, 92.7, 127.6, 127.7, 128.7, 129.1, 129.3, 138.7, 140.0, 162.1, 162.3. IR 1750, 1560 cm^{-1}. HRMS (M+NH_4) 410.959, calcd for $C_{12}H_{17}Br_2N_2O_4$ 410.955.

Ethyl 4-methyl-2-nitro-4-(trifluoromethyl)acetylpentanoate (99). Gem dimethyl ester **45** (30 mg, 0.17mmol) was stirred at rt overnight in 250 μL TFA. Dilution with ether followed by washing with water afforded after fcc 33 mg (0.11 mmol, 67 %) product. ^{1}H NMR: δ 1.25 (t, J = 7.2 Hz, 3 H), 1.45 (s, 6 H), 3.11 (s, 2 H), 4.23 (q, J = 7.2 Hz, 2 H), 6.42 (br, 1 H). IR 1780, 1730, 1600, 1380, 1170 cm^{-1}.

Reactions of Ethyl nitrocyclopropanecarboxylates

Preparation of Isoxazoline N-oxides by Isomerization of Ethyl nitrocyclopropanecarboxylates with Boron trifluoride etherate. For example 43 mg (0.23 mmol) ethyl 2,2-dimethyl-1-nitrocyclopropanecarboxylate (**45**) was dissolved in 0.5 ml methylene chloride and stirred in a 5 mL rbf. A few drops $BF_3{\cdot}Et_2O$ were added and the mixture was stirred for 1 h. TLC showed complete disappearance of **45** and a new spot that was much more polar had grown in. The mixture was diluted with 5 mL methyene chloride, washed with water, dried over magnesium sulfate and concentrated to yield 43 mg (100 %) of the pure isoxazoline N-oxide **100**.

Preparation of 100 by heating in DMSO. Compound **45** (100 mg, 0.53 mmol) was heated in 1 mL dry DMSO at 60 °C and periodically monitored by TLC. After 5 h, the rxn mixture was worked up and ^{1}H NMR analysis showed clean conversion of 60 % of the material to the product.

5,5-Dimethyl-3-ethyloxycarbonyl-4,5-dihydroisoxazole-N-oxide (100). ^{1}H NMR: δ 1.24 (t, J = 7.2 Hz, 3 H), 1.42 (s, 6 H), 3.09 (s, 2 H), 4.21 (q, J = 7.2 Hz, 2 H). ^{13}C NMR: δ 14.0, 26.8, 42.6, 61.6, 80.4, 109.3, 159.2. IR 1730, 1690, 1610, 1450 cm^{-1}. HRMS (M+H) 188.089, calcd for $C_7H_6NO_4$ 188.092.

3-Ethyloxycarbonyl-5-phenyl-4,5-dihydroisoxazole-N-oxide (101). ^{1}H NMR: δ 1.27 (t, J = 7.2 Hz, 3 H), 3.35 (dd, J = 7.9, 17.0 Hz, 1 H), 3.76 (dd, J = 9.6, 17.0 Hz, 1 H), 4.28 (q, J = 7.2 Hz, 2 H). 5.66 (dd, J = 7.9, 9.6 Hz, 1 H), 7.36 (m, 5 H). IR 1730, 1690, 1620 (br) cm^{-1}. HRMS (M+H) 236.089, calcd for $C_{11}H_{14}NO_4$ 236.092.

5,5-Diphenyl-3-ethyloxycarbonyl-4,5-dihydroisoxazole-N-oxide (102). ^{1}H NMR: δ 1.26 (t, J = 7.0 Hz, 3 H), 4.19 (s, 2 H), 4.26 (q, J = 7.0 Hz, 2 H), 7.13 - 7.52 (m, 10 H). IR 1740, 1700, 1640, 1550, 1500 cm-^{1}.

3-Cyano-5-phenyl-4,5-dihydroisoxazole-N-oxide (103). ^{1}H NMR: δ 3.33 (dd, J = 8.4, 16.4 Hz, 1 H), 3.63 ((dd, J = 9.5, 16.4 Hz, 1 H), 5.83 (t, J = 8.7 Hz, 1 H), 7.31-7.41 (m, 5 H). ^{13}C NMR: δ 37.2, 80.1, 92.7, 109.6, 125.3, 129.9, 135.9. IR 2220, 1620, 1555, 1500, 1460 cm^{-1}. HRMS (M+NH4) 206. 093, calcd for $C_9H_{12}N_3O_2$ 206.092.

5-Methyl-5-phenyl-3-phenylcarbonyl-4,5-dihydroisoxazole-N-oxide (104). ^{1}H NMR: δ 1.82 (s, 3 H), 3.54 (d, J = 15.0 Hz, 1 H), 3.66 (d, J = 15.0 Hz, 1 H), 7.23-7.50 (m, 8 H), 7.82-7.86 (m, 2 H). ^{13}C NMR: δ 29.7, 44.4, 74.2, 89.2, 124.1, 127.9, 128.0, 128.1, 128.8, 129.8, 132.0, 144.4, 162.5. IR 1630, 1600, 1490 cm^{-1}. HRMS (M+H) 282.111, calcd for $C_{17}H_{16}N0_3$ 282.113.

***cis,cis*- and *trans,trans*-2,3-Dimethyl-1-nitrocyclopropanecarboxylic acids (79 and 80).**[21] Sodium hydroxide (25 mg, 0.63 mmol, 0.26 eq)was added to 450 mg (2.41 mmol) of a 4:1 mixture of ethyl cis,cis-2,3-dimethyl-1-nitrocyclopropanecarboxylate (**48**) and ethyl trans,trans-2,3-dimethyl-1-nitrocyclopropanecarboxylate (**49**) in 3 ml 1:1 ethanol/water. The mixture was stirred at room temperature overnight. After diluting with 2 mL water and 10 ml methylene chloride, the organic layer was separated. The aqueous was extracted 3 x with 20 mL methylene chloride. The combined organic layers were dried and evaporated to yield 360 mg (1.93 mmol, 99%) of pure ethyl *cis,cis*-2,3-dimethyl-1-nitrocyclopropanecarboxylate (**48**). The aqueous layer was acidified to pH = 1 with hydrochloric acid and extracted 3 x with 20 ml methylene chloride. After drying and concentrating the organic fractions 75 mg (0.47 mmol, 98%) of **79** was obtained. ^{1}H NMR: δ 1.17 (m, 6 H), 2.06 (m, 2 H), 10.61 (br, 1 H). IR 3300-2700 (br), 1555, 1330 cm^{-1}. HRMS (M+NH_4) 177.088, calcd for $C_6H_{13}N_2O_4$ 177.087. Mp 154 - 156 °C. Anal. calcd for $C_6H_9NO_4$: C, 49.28; H, 5.70. Found: C, 49.34; H, 5.70.

Sodium hydroxide (240 mg, 6 mmol, 3.09 eq) was added to 360 mg (1.93 mmol) of ethyl *cis,cis*-2,3-dimethyl-1-nitrocyclopropanecarboxylate (**48**) in 6 ml 1:1 ethanol/water. The mixture was stirred for 24 h. After acidifying to pH = 1, the solution was extracted 3 x with 40 ml methylene chloride. The organic fractions were dried and evaporated to yield 305 mg (1.92 mmol, 99%) **80**. ^{1}H NMR: δ 1.22 (m, 6 H), 2.38 (m, 2 H), 11.47 (br, 1 H). ^{13}C NMR: δ 8.0, 30.2, 72.7, 167.9. IR 3300-2700 (br), 1555, 1330 cm^{-1}. Mp 96-98 °C.

***syn*-7-Nitrobicyclo[4.1.0]heptane-7-carboxylic acid (105).** Sodium hydroxide (36 mg, 0.9 mmol) was added to 180 mg (0.85 mmol) of a 6:1 diastereomeric mixture of esters **50** and **51** in 2 mL ethanol. After stirring at rt overnight, the mixture was concentrated, extracted with methylene chloride, dried and then concentrated to yield 30 mg (0.14 mmol) of the major (syn) ester **50**. The aqueous was acidified to pH = 1 with conc HCl ; extracted with methylene chloride and concentrated to afford 90 mg (0.49 mmol, 69 %) of the acid. ^{1}H NMR: δ 1.08 - 1.37 (m, 4 H), 1.95 (m, 4 H), 2.36 (m, 2 H), 8.96 (br, 1 H). ^{13}C NMR: δ 19.0, 20.2, 28.8, 72.2, 166.7. IR 3500 - 2600 (br), 1760, 1530, 1340 cm^{-1}. HRMS (M+NH4) 203.103, calcd for $C_8H_{15}N_2O_4$ 203.103. Mp 133-134 °C. Anal. calcd for $C_8H_{11}NO_4$: C, 51.89; H, 5.99. Found: C, 51.96; H, 6.04.

Hydrolysis of Nitrocyclopropanecarbonitriles

2,2,3,3-Tetramethyl-1-nitrocyclopropanecarboxamide (106).[21] The partial hydrolysis of **41** to **106** was performed according to a literature procedure.[43] Thus 1.4 mL 30 % H_2O_2 was added to a stirred mixture of 480 mg (2.86 mmol) nitrocyclopropanecarbonitrile **41**, 200 mg tetrabutylammonium hydrogen sulfate and 1 mL 20 % sodium hydroxide solution in 1 ml methylene chloride. The mixture was stirred for 2 h at 0 °C, diluted with methylene chloride, washed, dried, concentrated and chromatographed (0 to 100 % EtOAc) to afford 140 mg (0.75 mmol, 26%) of amide **106.** ^{1}H NMR: δ 1.16 (s, 6 H), 1.23 (s, 6 H), 6.0 (br, 2 H). ^{13}C NMR: δ 18.6, 19.6, 31.2, 81.9, 164. IR 3500, 3400, 1710, 1535 cm^{-1}. HRMS (M+H) 187.106, calcd for $C_8H_{15}N_2O_3$ 187.108. Mp 123 - 125 °C.

***cis,cis*-2,3-Dimethyl-1-nitrocyclopropanecarboxamide (82).** In a similar fashion 105 mg (0.66 mmol, 46 %) of amide were obtained from 200 mg (1.42 mmol) nitrile **39** after concentration, chromatography and crystallization. ^{1}H NMR: δ 1.22 (m, 6 H), 2.37 (m, 2 H), 5.80 - 6.19 (br, 2 H). ^{13}C NMR: δ 8.7, 30.6, 72.9, 162.9. IR 3500, 3400, 1710, 1540 cm^{-1}. HRMS (M+H) 159.077, calcd for $C_6H_{11}N_2O_3$ 159.079. Mp 109 - 111 °C.

2-Butyl-1-nitrocyclopropanecarboxamide (3:1 mixture of cis/trans isomers) (107 and 108). This material was obtained in a 75% yield from a 3:1 mixture of nitriles **37** and **38.** ^{1}H NMR: δ .81 (m, 3 H), 1.13 - 1.57 (m, 7 H), 1.92 (m, 1 H), 2.16 (m, 1 H), 6.51 (br, 1 H), 7.47 (br, 1 H). ^{13}C NMR: δ 13.7, 13.8, 22.1, 23.0, 24.1, 26.6, 26.7, 30.3, 30.7, 35.2, 37.6, 70.9, 72.1, 162.2, 166.6. IR 3500 - 3200 (br), 1690, 1540, 1360 cm^{-1}. HRMS (M+NH4) 204.132, calcd for $C_8H_{18}N_3O_2$ 204.135.

2,2-Dimethyl-1-nitrocyclopropane methanol (109). Gem dimethyl ester **45** (180 mg, 1 mmol) was dissolved in 5 mL ether. This solution was cooled in an ice bath and $LiAlH_4$ (60 mg, 1.5 mmol) was added. After stirring for 30 min, TLC showed complete consumption of starting material and a more polar spot had appeared. After quenching with water, extracting with ether, washing, drying and evaporation pure product was obtained (120 mg, 0.83 mmol, 83%). ^{1}H NMR: δ 1.02 (d, J = 6.3 Hz, 1 H), 1.12 (s, 3 H), 1.25 (s, 3 H), 1.90 (d, J = 6.3 Hz, 1 H), 3.0 (br, 1 H), 3.94 (d, J = 13.5 Hz, 1 H), 4.12 (d, J = 13.5 Hz, 1 H). ^{13}C NMR: δ 19.6, 22.1, 26.3, 28.7, 63.4, 75.8. IR 3500-3300 (br), 1540, 1350 cm^{-1}. HRMS (M+H) 146.084, calcd for $C_6H_{12}NO_3$ 146.082.

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References and Notes.

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