Synthesis of α-Nitro-α-diazocarbonyl Derivatives and Their Applications in the Cyclopropanation of Alkenes and in O–H Insertion Reactions

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

A facile and highly efficient method for the preparation of α-nitro-α-diazocarbonyl derivatives by a diazo-transfer reaction involving (trifluoromethyl)sulfonyl azide has been developed. These substrates undergo a rhodium-catalyzed cyclopropanation reaction with a variety of alkenes. A systematic study of the reaction indicated that the diastereoselectivity of the cyclopropanation could be effectively controlled through the modification of the steric bulk of the diazo reagent. A novel O–H insertion reaction of the metal–carbene complex derived from the α-nitro-α-diazocarbonyl reagent afforded the corresponding novel α-nitro-α-alkoxy carbonyl derivatives.

Introduction. – In recent years, diazo carbonyl chemistry [1] has been extensively exploited in several transformations such as in C–H insertions, cyclopropanations[1]), cascade reactions [3], X–X (Br–Br, I–I) [4] and Y–H insertions (Y = O, N, S, P, Se, Si)[2]), epoxidations [6], aziridinations [7], and in rearrangements or transfer reactions involving ylides[3]). The largest body of literature encompasses the chemistry of α-diazo carbonyl, α-alkyl/aryl-α-diazocarbonyl, or α-vinyl-α-diazocarbonyl reagents, and it demonstrates exceptional versatility. Our research group has recently become interested in the preparation and synthetic applications of α-nitro-α-diazo carbonyls for the expedient synthesis of 2-substituted 1-aminocyclopropanecarboxylic acids (**1**) by reduction of the corresponding α-nitrocyclopropanecarboxylic acid **2** (*Scheme 1*)[4]). Additionally, the nitro compound could serve as a possible useful synthon towards the preparation of isoxazoline *N*-oxides **3** [10][5]), leading to γ-hydroxyamino acids **4** [11] or other γ-substituted amino acids **5** (*Scheme 1*) [12].

The simplest member of the class of constrained α-amino acids is the naturally occurring 1-aminocyclopropanecarboxylic acid (ACC, **6**)[6]). ACC, a natural plant growth hormone [14], was found to be a precursor for the biosynthesis of ethylene.

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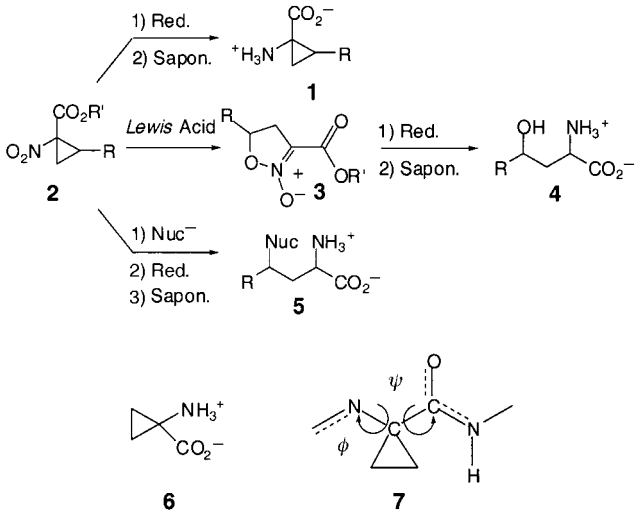
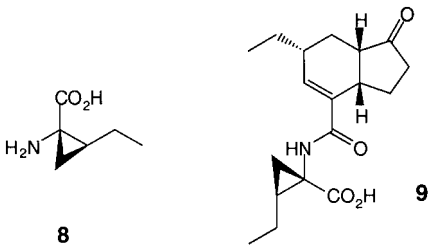
[1]) For a review, see [2].
[2]) For a review, see [5a]; for examples of N–H insertions, see [5b,c].
[3]) For reviews, see [8].
[4]) For R = H, see [9].
[5]) See also [23].
[6]) First isolation, see [13].

Scheme 1



Applications of ACCs include their introduction into peptides to effect a change in the N–C–C–O dihedral angle relative to that of natural amino acid units in the peptide. The rigidity of the cyclopropane ring favors small ϕ and ψ angles (**7**), which leads to compact folded peptide conformations[7]). The resulting dense structures strongly decrease the rate of enzymatic peptide hydrolysis, which is of significant importance in the design of peptidomimetics [16]. Inhibitors of EFE (ethylene-forming enzyme), amino transferase, tryptophane hydrolase, Dopa decarboxylase, histidine decarboxylase, and carboxypeptidase are also found to contain this unique class of ACCs [17].

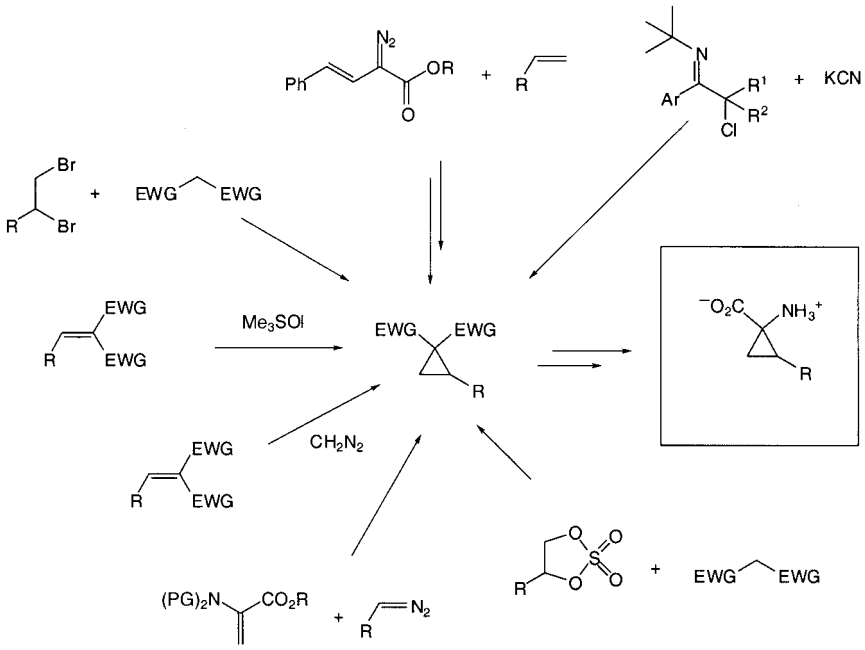
In addition, (+)-coronamic acid (**8**) [18], a subunit found in coronatine (**9**), is a natural product isolated from *Pseudomonas syringae, pv atropurpurea* [19], which was shown to induce the chlorosis of Italian rye grass leaves.



The presence of ACC subunits in nature along with its incorporation into bioactive compounds has stimulated the interest for further development of synthetic methodologies to access them in enantiomerically enriched form. Numerous approaches have been reported for the preparation of substituted ACCs [20], however, only a few

7) For recent incorporation of ACC into peptides, see [15].

Scheme 2



EWG = Electron withdrawing group, *i.e.*, COOR, CN, NC, $(PG)_2N$; PG = protecting group.

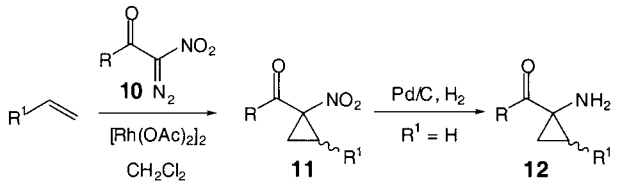
methods allow the stereoselective preparation of all possible stereoisomers (*Scheme 2*) [7][21].

Improvements on existing methodologies could provide a more direct synthesis of ACC derivatives that avoids extensive functional-group differentiations and manipulations. With this in mind, a direct incorporation of an 'amino acid synthetic equivalent' into an alkene *via* a transition metal catalyzed diazo decomposition appeared to be the most effective way. We, thus, examined a number of possibilities, including imino, phthalimido, and nitrodiazocarbonyl reagents as amine equivalents, which could be quickly transformed to the desired amine [22]. A survey of the literature indicates that precedents exist in cyclopropanation reactions involving α-nitro-α-diazocarbonyl reagents (**10**) as 'amino acid equivalents'[8]). The approach adopted by *O'Bannon* and *Dailey* employs the decomposition of diazo compounds by $[Rh(OAc)_2]_2$ in the presence of an alkene to afford substituted 1-nitrocyclopropanecarbonyls **11** (*Scheme 3*) [23]. *Seebach* and *Häner* showed that hydrogenation of **2** (R = H) (= **11**: R = OR′, R^1 = H), followed by saponification provided **1** (= **12**: R = OH, R^1 = H) [9].

Surprisingly, there are relatively few reported examples of other nitrocarbenes in the literature [24]. In this publication, we report on a more practical method for the preparation of α-nitro-α-diazocarbonyl reagents **10**, and we describe our efforts to optimize the diastereoselectivity in the transition metal catalyzed cyclopropanation of

[8]) For transition metal catalyzed cyclopropanations, see [23].

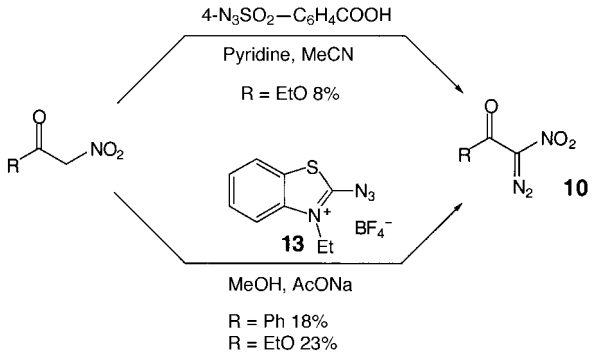
Scheme 3



alkenes with these reagents. Our ultimate goal will be to access either diastereoisomers of **11** by varying the structure of the starting diazo reagent or of the catalyst. In the second part, we describe the novel O–H insertion of the corresponding metal α-nitrocarbonyl–carbene complexes.

Results and Discussion. – *Preparation of α-Nitro-α-diazo Carbonyl Reagents.* To the best of our knowledge, there are only two reports of the preparation of α-nitro-α-diazo esters *via* a diazo-transfer process. *Hendrickson* and *Wolf* [25] showed that ethyl α-nitro-α-diazoacetate can be prepared in 8% yield by mixing ethyl nitroacetate with 4-(azidosulfonyl)benzoic acid. Alternatively, *Balli* and *Löw* showed that the use of thiazolium azide **13** leads to a slightly more efficient diazo transfer reaction (*Scheme 4*) [26].

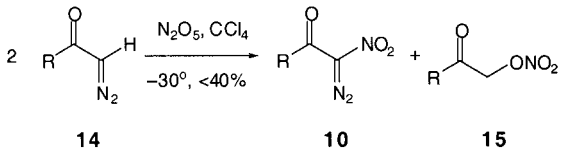
Scheme 4



Schöllkopf and co-workers developed a more efficient method of accessing α-nitro-α-diazo esters and ketones involving the treatment of diazo compounds **14** with the strong nitrating reagent N_2O_5 (*Scheme 5*) [24]. However, the preparation of N_2O_5 is tedious since it decomposes above $-30°$. Furthermore, two equivalents of the starting diazo compound are required, the second being consumed when acting as a base to deprotonate the intermediate diazonium ion.

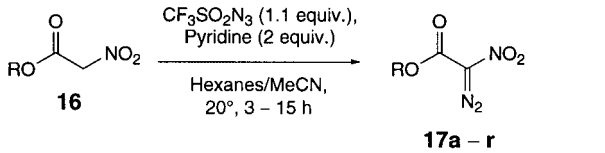
Due to the inherent disadvantages associated with the existing methodologies, we developed an improved procedure for the facile and general preparation of these reagents. We previously reported [27] a novel diazo-transfer reaction involving the treatment of a MeCN/hexanes solution of (trifluoromethyl)sulfonyl (trityl) azide [28] and an α-nitro ester or ketone with pyridine, which affords the corresponding α-nitro-

Scheme 5

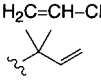


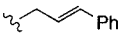
α-diazo ester **17** and ketone **10** in high yields. The diazo transfer proceeds smoothly for a large variety of alkyl substituents as α-nitro ester substrates **16** (*Scheme 6*), providing the desired compounds in generally $>80\%$ yield.

Scheme 6. *Diazo-Transfer Reaction on α-Nitro Esters.* Isolated yields after chromatography in parentheses.



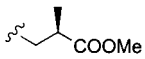
17a (90%, at 0°) R = Me
b (92%) R = Et
c (86%) R = i-Pr
d (90%) R = *t*-Bu
e (88%) R = H_2C=CH–CH_2


f (73%) R =


g (81%) R = Ph

h (96%) R = $PhCH_2$


i (72%) R =

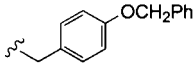

j (68%) R = COOMe


k (87%) R =

17l (86%) R =


SiMe3

m (85%) R =

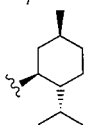

OCH2Ph

n (61%) R =

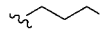

Ph

o (96%) R =

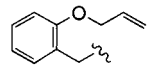
p (99%) R =



q (83%) R =


Br

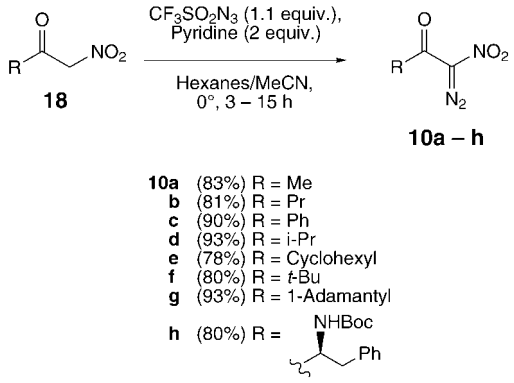
r (99%) R =


O

Isolation of the α-nitro-α-diazo carbonyl compound from the reaction medium involves simple concentration of the solvent under reduced pressure followed by flash chromatography on silica gel with $CHCl_3$ as eluent. The product elutes as a yellow band and can be followed visually. Direct diazo transfer on nitroacetic acid is unsuccessful as it decarboxylates in the presence of pyridine.

Under the same conditions, the diazo-transfer reaction also affords, in modest to high yields, the corresponding α-nitro-α-diazo ketones **10a**–**h** starting from α-nitro ketone **18** (*Scheme 7*). However, it was realized that the yields of the diazo-transfer reaction could be substantially increased relative to those originially reported [27] by addition of pyridine at 0° instead of room temperature. Presumably, the slight

Scheme 7. *Diazo-Transfer Reaction on α-Nitro Ketones.* Yields in parentheses.



decomposition of the α-nitro ketone substrates in the presence of pyridine is reduced at lower temperatures.

It should be mentioned that *tert*-butyl diazo ketone **10f** decomposes at a moderate rate (in 24 h) if not stored in the freezer[9]). The crystal structure of methyl α-nitro-α-diazoacetate (**17a**) was obtained (*Fig. 1*)[10]).

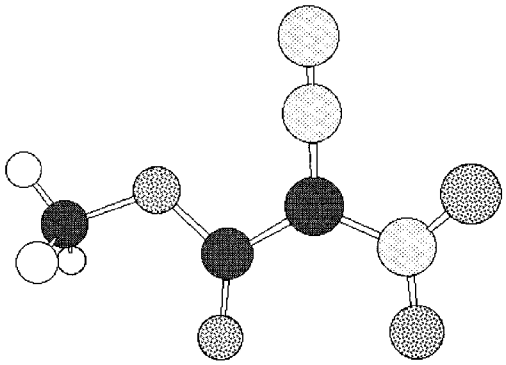


Fig. 1. *Chem 3D representation of the crystal structure of methyl diazonitroacetate* (**17a**)

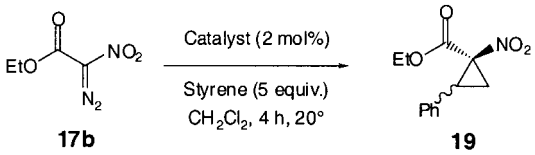
Cyclopropanation Reaction Catalyzed by Dirhodium Catalysts. Surprisingly, there have been few reports of catalysts other than $[Rh(OAc)_2]_2$ for the cyclopropanation reaction involving α-nitro-α-diazo carbonyl reagents. We were, thus, interested in studying ligand effects on the diastereoselectivity and yield of the cyclopropanation reaction for a given set of alkene/diazo reagents. A series of achiral dirhodium-based catalysts were tested for their catalytic activity in a model system based on ethyl

[9]) α-Nitro-α-diazo carbonyl derivatives should be handled with great care due to their explosive nature. In our hands, methyl ester **17a** was found to be quite shock-sensitive.

[10]) For the X-ray crystal structure of α-nitro-α-diazoacetic acid, see [29].

α-nitro-α-diazoacetate (**17b**) and styrene (*Scheme 8*). A variety of commercially available dirhodium(II)carboxamidate catalysts including $Rh_2(cap)_4$ (*Table 1*, *Entry 1*), $Rh_2((5R)\text{-MEPY})_4$, $Rh_2((4S)\text{-MEOX})_4$, and $Rh_2((4S)\text{-MPPIM})_4$ were found to lead only to decomposition or recovery of the diazo substrate under a variety of conditions. $[Rh((4S)\text{-MEAZ})_2]_2$ [30] proved to be an exception, and cyclopropanation results with this catalyst have been previously reported by us in work involving asymmetric cyclopropanations [31]. The focus then turned to various dirhodium(II) carboxylate catalysts. An electron-withdrawing ligand (*Table 1*, *Entry 2*) was found to give low yields of the corresponding cyclopropane **19** and a surprising recovery of 41% of the diazo substrate. Sterically undemanding, electron-rich ligands (*Entries 3* and *4*) were found to give higher yields of the desired cyclopropane. Further improvements in the yields resulted with sterically demanding, electron-rich ligands (*Entries 5* and *6*). In all cases, the *trans*-diastereoisomers were strongly favored.

Scheme 8



17b **19**

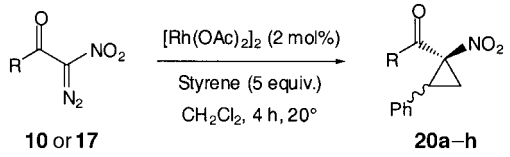
Table 1. *Cyclopropanation Reaction with Dirhodium(II) Carboxamidates and Carboxylates*

Entry	Catalyst	Yield of **19** [%][a])	*cis*/*trans*
1	$[Rh(cap)_2]_2$[b])	dec.	–
2	$[Rh(CF_3CO_2)_2]_2$	24	8 : 92
3	$[Rh(OAc)_2]_2$	79	12 : 88
4	$[Rh(C_7H_{15}CO_2)_2]_2$	76	10 : 90
5	$[Rh(t\text{-}BuCO_2)_2]_2$	84	15 : 85
6	$[Rh(Adaman)_2]_2$[c])	90	12 : 88

[a]) Combined yield (*cis*/*trans*) after column chromatography. [b]) cap: caprolactam. [c]) Adaman: adamantane-1-carboxylate.

cis/trans-*Selectivity as a Function of the Diazo Reagent*. We then set out to study the substituent effect of the α-nitro-α-diazocarbonyl substrate on the *cis*/*trans* selectivity. We tested a number of cyclopropanation reactions with styrene as a substrate and varied the size of the ester or ketone substituent (*Scheme 9*, *Table 2*).

Scheme 9



10 or **17** **20a–h**

Table 2. *Diastereoselectivity as a Function of the Diazo Reagent*

Entry	Product	R	Yield [%][a])	*cis*/*trans*
1	**20a**	MeO	78	9 : 91
2	**20b**	EtO	80	12 : 88
3	**20c**	i-PrO	78	25 : 75
4	**20d**	*t*-BuO	81	45 : 55
5	**20e**	Me	77	22 : 78
6	**20f**	Pr	74	19 : 81
7	**20g**	Ph	74[b])	84 : 16
8	**20h**	*t*-Bu	55[b])	80 : 20

[a]) Isolated yields after column chromatography. [b]) 15% (*Entry 7*) and 30% (*Entry 8*) yield of the corresponding isoxazoline *N*-oxides resulting from cyclopropane opening were found as by-products.

A highly diastereoselective cyclopropanation favoring the *trans*-cyclopropanes **20** (the Ph group in 2-position is *trans* to the NO_2 group) can be obtained when employing a sterically minimally demanding group. With the methyl ester, a *cis*/*trans*-ratio of 9 : 91 was obtained (*Entry 1*) while a *cis*/*trans*-ratio of 12 : 88 was obtained with the ethyl ester (*Entry 2*). Increasing alkyl-group steric bulk on the ester leads to loss of this diastereoselectivity (*Entries 3* and *4*) resulting in almost equal preference of the two diastereoisomers in the case of the *tert*-butyl ester (*Entry 4*). The use of moderately bulky α-nitro-α-diazo ketones as substrates can produce a *cis*-selective product with *cis*/*trans*-ratios of up to 84 : 16 (*Entry 7*). These diastereoisomers can be readily separated by column chromatography as is the case with the less-bulky esters. The absolute configuration is in agreement with previously reported findings [23] and was further confirmed by the crystal structure of *trans*-1-[2-(4-fluorophenyl)-1-nitro-cyclopropyl]-ethanone.

It is also noteworthy to mention that increasing the steric bulk of the ketones decreases the stability of the cyclopropanes. In the case of 1-adamantyl and cyclohexyl derivatives, isolated yields ranged from 20 to 30%; most of the material was recovered as the isoxazoline oxides after silica-gel chromatography (**21**, *Scheme 10*) [23]. Presumably, release of ring strain is the driving force of this rearrangement.

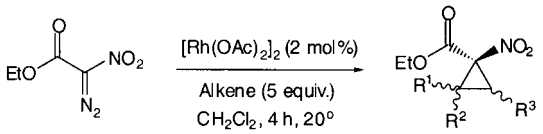
Scheme 10

20 **21**

Cyclopropanation of Various Alkenes. The cyclopropanation reaction is known to proceed with a variety of alkenes (*Scheme 11*). It is generally believed that the highest yields can be obtained with electron-rich, terminal, and *cis*-configured olefins (*Table 3*, *Entries 1 – 4*). Surprisingly, however, when the cyclopropanation reaction was performed with more-electron-deficient substrates such as 2-bromopropene and α-bromostyrene (*Entries 5* and *6*), the corresponding cyclopropanes were afforded in

modest yields[11]). β-Bromostyrene was also submitted to the same reaction conditions, and the cyclopropanation afforded low yields suggesting the necessity for the appropriate polarization in the substrate. Considering a concerted formation of the nitrocyclopropanecarboxylate as proposed by *Doyle et al.* [33] for related systems, the polarization of the β-bromostyrene would result in a destabilization of the intermediates, thus, decreasing cyclopropane formation.

Scheme 11



17b **22**

Table 3. *Scope of Cyclopropanation with* **17b**

Entry	Alkene	Product	R^1	R^2	R^3	Yield [%]	*cis*/*trans*
1	α-Methylstyrene	**22a**	Ph	Me	H	95	72 : 28[a])
2	1,1-Diphenylethene	**22b**	Ph	Ph	H	60[b])	–
3	1*H*-Indene	**22c**	H	$-2\text{-}CH_2-C_6H_4-$		84	97 : 3[c])
4	1-Hexene	**22d**	Bu	H	H	40	40 : 60
5	2-Bromopropene	**22e**	Br	Me	H	50	80 : 20
6	α-Bromostyrene	**22f**	Br	Ph	H	77	75 : 25

[a]) Cyclopropane/isoxazoline oxide. [b]) Yield of isoxazoline oxide [c]) *exo*/*endo* with respect to NO_2.

Cyclopropane **22b** completely rearranged to the corresponding isoxazoline oxide on silica gel while the rearrangement of **22a** was much slower. This effect probably arises from the ability of the substituents to stabilize a partial positive charge in the benzylic position. Accordingly, cyclopropanes **22c**–**f** were not found to show rearrangement products. Strong electron-donating groups on an aryl ring can also facilitate the rearrangement, thus, the cyclopropane resulting from the reaction with 4-methoxystyrene gives only isoxazoline oxide when exposed to silica gel. The structure of the cyclopropane **22c** derived from the reaction with 1*H*-indene (*Entry 3*) was confirmed by X-ray crystallography of the corresponding methyl ester showing the NO_2 group *exo* to the ring as the predominant isomer (*Fig. 2*).

O–H Insertions. As part of our continuing interest in the chemistry of α-nitro-α-diazo carbonyl substrates, we wondered if they could potentially undergo O–H-insertion reactions, yielding the 'novel' α-nitro-α-alkoxy carbonyl derivatives [34]. The substrates **23** could then be reduced to serve as valuable precursors for alkoxy glycines [35]. Since the pioneering work of *Teyssié* and co-workers on the Rh-catalyzed insertion of ethyl diazoacetate in the O–H bond of alcohols [36], the use of Rh catalysts has been largely investigated [5]. In a similar fashion, rhodium(II) acetate is also an extremely effective catalyst for the novel conversion of these α-nitro-α-

[11]) For an ethyl diazoacetate cyclopropanation of α-fluorostyrene, see [32].

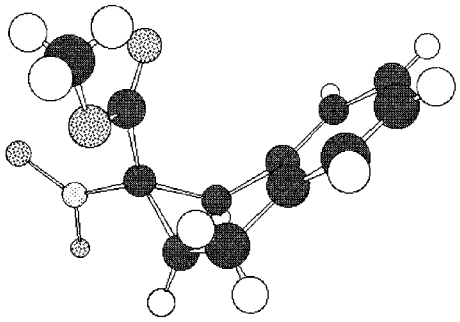


Fig. 2. *Chem 3D representation of the crystal structure of methyl* exo-*1,1a,6,6a-tetrahydro-1-nitrocyclopropa[a]indene-1-carboxylate*

diazocarbonyl substrates **10** or **17** into α-alkoxy-α-nitrocarbonyls **23** (*Scheme 12*). The intermolecular O–H-insertion reaction is possible with a range of primary to tertiary alcohols (*Table 4*).

Scheme 12

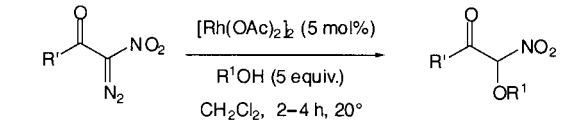


Table 4. *O–H Insertion of Alcohols*

Entry	Substrate	Product	R^1	Yield [%][a])
1	**17b**	**23a**	$H_2C{=}CH{-}CH_2$	84
2	**17b**	**23b**	$PhCH_2$	99
3	**17b**	**23c**	*t*-Bu	45
4	**17b**	**23d**	Cyclopropylmethyl	87
5	**17b**	**23e**	(*R*)-2-(Methoxycarbonyl)propyl	74[b])
6	**17h**	**23f**	$H_2C{=}CH{-}CH_2$	92
7	**17h**	**23g**	$PhCH_2$	84
8	**17h**	**23h**	Menthyl[c])	79[d])
9	**10c**	**23i**	$H_2C{=}CH{-}CH_2$	78

[a]) Isolated yields after chromatography. [b]) Isolated as a 50 : 50 mixture of diastereoisomers. [c]) (1*R*,2*S*,5*R*)-Menthyl. [d]) Isolated as a 55 : 45 mixture of diastereoisomers.

In the case of allyl alcohol, we did not observe any competing cyclopropanation (*Entries 1*, *6*, and *9*) for substrates **17b**, **17h**, and **10c**. The use of chiral alcohols such as (–)-(1*R*,2*S*,5*R*)-menthol did not lead to high stereoinduction with a diastereoisomer ratio of 55 : 45 at the created α-center (*Entry 8*).

Due to the complete chemoselectivity with the allyl alcohol as a substrate we decided to examine the relative rates of O–H insertion *vs.* cyclopropanation in a competition experiment (*Scheme 13*). Substrate **17b**, styrene, and various alcohols

were used to determine the relative rates of cyclopropanation products **20** *vs.* O–H-insertion products **23** (*Table 5*). The cyclopropanation of styrene is preferred over O–H insertion in the case of *t*-BuOH (*Entry 1*), while cyclopropanation and O–H insertion proceed at similar rates when styrene and i-PrOH are compared (*Entry 2*). Finally, the O–H-insertion pathway dominates when the primary $PhCH_2OH$ is used (*Entry 3*). This behavior follows trends observed with ethyl diazoacetate.

Scheme 13

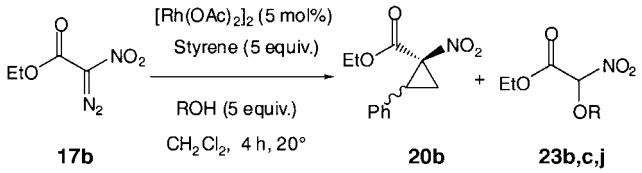


Table 5. *O–H Insertion* vs. *Cyclopropanation Competition Experiments*

Entry	Product **23**	R	Cyclopropanation/O–H insertion	Yield of **20b** + **23** [%][a])
1	**23c**	*t*-Bu	10 : 1	77
2	**23j**	i-Pr	1 : 1	78
3	**23b**	$PhCH_2$	1 : 4	94

[a]) Isolated yields after chromatography based on theoretical yield of product from crude ratios.

Conclusions. – In summary, the yields for the preparation of α-nitro-α-diazo carbonyl substrates with trityl azide as a diazo-transfer reagent can be substantially improved by simply cooling the reaction media to 0° during pyridine addition. The wide range of substrates accessible by this method allowed us to effectively control the diastereoselectivity in the cyclopropanation with styrene affording either *cis*- or *trans*-diastereoisomers preferentially. The cyclopropanation occurs with modest to high yields with a variety of alkene substrates including bromo alkenes, which are typically low-yielding for other diazo derivatives.

A highly efficient method for the preparation of the novel α-alkoxy-α-nitro carbonyl derivatives from the corresponding α-nitro-α-diazo carbonyl compounds by a novel $[Rh(OAc)_2]_2$ catalyzed O–H insertion with the desired alcohol is also reported. The applications of these compounds are currently investigated and will be reported in due course along with an improved method for enantioselective cyclopropanations.

Experimental Part

General. Unless otherwise mentioned, all reactions were carried out under Ar atmosphere with oven-dried glassware. All solvents were dried on a *GlassContour* system (*Irvine*, CA). Pyridine was distilled from CaH_2 while (trifluoromethyl)sulfonyl anhydride was distilled from P_2O_5. Column chromatography: flash chromatography (FC) with the indicated solvent system on *Silicycle* silica-gel (230–400 mesh) according to the method of *Still et al.* [37]. M.p.: *Thomas-Hoover* melting point apparatus, in open capillaries, uncorrected. IR: *Perkin-Elmer 783*; only the most important and relevant frequencies are reported. ^{1}H-NMR: *Bruker AMX-300* or *AMX-R-400*; at 400 MHz in $CDCl_3$, if not stated otherwise; chemical shifts δ in ppm from an internal standard of residual $CHCl_3$ (7.27 ppm); J in Hz. ^{13}C-NMR: *Bruker ARX-400*; at 100 MHz in $CDCl_3$, if not stated

otherwise; chemical shifts δ in ppm relative to the central line of the triplet at 77.23 ppm for $CDCl_3$. Full assignment of chemical shifts was confirmed by DEPT experiments. HR-MS: obtained from the Centre régional de spectrométrie de masse de l'Université de Montréal; *Kratos MS50*; *m/z*. Combustion analyses were performed by the Laboratoire d'analyse élémentaire of the Université de Montréal.

Synthesis of α-Nitro Esters **16**. Prepared according to the procedure reported by *Mioskowski* and co-workers [38]. **16a** and **b** are commercially available from *Aldrich*, **16d**,**e**,**h**,**p** [38], **16k** [39], **16l** [31], **16c**,**g**,**i**,**m**,**n**,**r** [27] have been previously reported.

1,1-Dimethylallyl 2-Nitroacetate (**16f**): 334 mg (33%). Pale yellow oil. IR (film): 1751*s*, 1563*s*. ^{1}H-NMR: 1.58 (*s*, 6 H); 5.09 (*s*, 2 H); 5.16 (*d*, J = 10.4, 1 H); 5.24 (*d*, J = 17.5, 1 H); 6.07 (*dd*, J = 17.5, 10.9, 1 H). ^{13}C-NMR: 26.3; 77.2; 85.3; 114.6; 140.7; 160.5. Anal. calc. for $C_7H_{11}NO_4$ (173.17): C 48.55, H 6.40, N 8.09; found: C 48.55, H 6.47, N 8.31.

Methyl (R)-2-Methyl-3-[(2-nitroacetyl)oxy]propanoate (**16j**): 150 mg (73%). Yellow oil. IR (film) 1760*s*, 1737*s*, 1567*s*, 1340*s*. ^{1}H-NMR: 1.23 (*d*, J = 7.2, 3 H); 2.86 (*m*, 1 H); 3.72 (*s*, 3 H); 4.35 (*dd*, J = 10.9, 5.5, 1 H); 4.44 (*dd*, J = 10.9, 7.4, 1 H); 5.17 (*s*, 2 H). ^{13}C-NMR: 13.7; 38.8; 52.2; 67.8; 76.2; 161.8; 173.7.

(1S,2S,4R)-1,3,3-Trimethylbicyclo[2.2.1]hept-2-yl 2-Nitroacetate (**16o**): 283 mg (59%). Colorless oil. IR (film): 1751*s*, 1565*s*. ^{1}H-NMR: 0.81 (*s*, 3 H); 1.07 (*s*, 3 H); 1.12 (*s*, 3 H); 1.22–1.25 (*m*, 1 H); 1.44–1.77 (*m*, 6 H); 4.51 (*s*, 1 H); 5.20 (*s*, 2 H). ^{13}C-NMR: 19.4; 20.1; 25.8; 26.5; 29.7; 39.9; 41.4; 48.3; 48.6; 76.5; 89.8; 162.3. HR-MS 241.13176 ($C_{12}H_{19}NO_4^+$; calc. 241.13141).

3-Bromopropyl 2-Nitroacetate (**16q**): 528 mg (75%). Pale yellow oil. IR (film): 1755*s*, 1563*s*. ^{1}H-NMR: 2.24 (*quint.*, J = 6.2, 2 H); 3.45 (*t*, J = 6.4, 2 H); 4.43 (*t*, J = 6.0, 2 H); 5.19 (*s*, 2 H). ^{13}C-NMR: 28.8; 31.3; 64.9; 76.3; 161.8.

Synthesis of the α-Nitro Ketones **18**: Prepared according to the procedure reported by *Baker* and *Putt* for **18a**,**c**,**d**,**g** [40], *Simmons et al.* for **18b** [41], **18e**,**f** [27], or *Yuasa et al.* for **18h** [42].

3-Methyl-1-nitrobutan-2-one (**18d**): 1.26 g (59%). Clear, colorless oil. IR (film): 1732*s*, 1560*s*. ^{1}H-NMR: 1.20 (*d*, J = 6.9, 6 H); 2.72 (*sept.*, J = 6.9, 1 H); 5.38 (*s*, 2 H). ^{13}C-NMR: 17.9; 39.8; 81.9; 199.8. HR-MS: 131.05819 ($C_5H_9NO_3^+$; calc. 131.05824).

1-(Adamant-1-yl)-2-nitroethanone (**18g**): 4.25 g (86%). White platelets. M.p. 82°. IR (film): 1703*s*, 1547*s*. ^{1}H-NMR: 1.69–1.86 (*m*, 11 H); 2.11 (*br*, 4 H); 5.44 (*s*, 2 H). ^{13}C-NMR: 27.8; 27.9; 36.3; 36.4; 36.6; 37.9; 38.9; 46.7; 80.1; 200.8. HR-MS: 223.12059 ($C_{12}H_{17}NO_3^+$; calc. 223.12084).

Typical Procedure for the Preparation of the α-Nitro-α-diazo Carbonyls.

CAUTION: Although we have not experienced any problems in the handling of these compounds ((trifluoromethyl)sulfonyl azide and the α-nitro-α-diazo carbonyl derivatives), extreme care should be taken when manipulating them due to their explosive nature.

Preparation of Trifluoromethylsulfonyl Azide Solution: According to *Fritschi* and *Vasella* [28].

Synthesis of α-Nitro-α-diazo Esters **17**. Prepared according to the previously reported procedure in [27]. Compounds **17a**–**e**,**g**,**i**,**l**,**m**,**n**,**p**,**r** have been previously reported [27][31].

1,1-(Dimethyl)allyl 2-Diazo-2-nitroacetate (**17f**): 89 mg (73%). Yellow oil. IR (film): 2143*s*, 1744*s*, 1698*s*, 1515*s*, 1320*s*. ^{1}H-NMR: 1.64 (*s*, 6 H); 5.19 (*d*, J = 10.9, 1 H); 5.29 (*d*, J = 17.4, 1 H); 6.13 (*dd*, J = 17.4, 10.9, 1 H). ^{13}C-NMR: 26.6; 86.1; 114.8; 140.8; 154.1. HR-MS: 199.058979 ($C_7H_9N_3O_4^+$; calc. 199.059306).

Benzyl 2-Diazo-2-nitroacetate (**17h**): 98 mg (96%). Yellow oil. IR (film): 2149*s*, 1746*s*, 1703*s*, 1520*s*. ^{1}H-NMR: 5.36 (*s*, 2 H); 7.40 (br., 5 H). ^{13}C-NMR: 68.5; 101.8 (CN_2); 128.9; 129.0; 129.3; 134.3; 155.5. HR-MS: 221.043867 ($C_9H_7N_3O_4^+$; calc. 221.043656).

Methyl (R)-3-[(2-Diazo-2-nitroacetyl)oxy]-2-methylpropanoate (**17j**): 84 mg (68%). Yellow oil. IR (film): 2152*s*, 1741*s*, 1520*s*. ^{1}H-NMR: 1.25 (*d*, J = 7.2, 3 H); 2.86–2.92 (*m*, 1 H); 3.72 (*s*, 3 H); 4.94–4.47 (*m*, 2 H). ^{13}C-NMR: 13.6; 38.9; 52.2; 67.4; 101.7 (CN_2); 155.1; 173.6. HR-MS: 232.05580 ($[M+1]^+$, $C_7H_9N_3O_6$; calc. 232.05696).

(3-Methyloxetan-3-yl)methyl 2-Diazo-2-nitroacetate (**17k**): 114 mg (87%). Yellow oil. IR (film): 2150*s*, 1747*s*, 1703*s*, 1520*s*, 1323*s*. ^{1}H-NMR: 1.32 (*s*, 3 H); 4.37 (*s*, 2 H); 4.39 (*s*, 2 H); 4.44 (*s*, 1 H); 4.46 (*s*, 1 H). ^{13}C-NMR: 20.9, 39.3; 70.7; 79.2; 102.0 (CN_2); 155.6.

(1S,2S,4R)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl 2-Diazo-2-nitroacetate (**17o**): 179 mg (96%). Yellow solid. M.p. 46°. IR (solid): 2145*s*, 1748*s*, 1698*s*, 1522*s*, 1323*s*. ^{1}H-NMR: 0.83 (*s*, 3 H); 1.08 (*s*, 3 H); 1.13 (*s*, 3 H); 1.15–1.17 (*m*, 1 H); 1.23–1.27 (*m*, 1 H); 1.55–1.45 (*m*, 1 H); 1.79–1.60 (*m*, 4 H); 4.59 (*d*, J = 1.9, 1 H). ^{13}C-NMR: 19.4; 20.3; 25.8; 26.6; 29.6; 39.8; 41.3; 48.2; 48.6; 89.8; 101.8 (CN_2); 155.9.

3-Bromopropyl 2-Diazo-2-nitroacetate (**17q**): 170 mg (99%). Yellow oil. IR (film): 2148*s*, 1746*s*, 1705*s*, 1515*s*, 1322*s*. ^{1}H-NMR: 2.24 (*quint.*, J = 6.3, 2 H); 3.45 (*t*, J = 6.3, 2 H); 4.44 (*t*, J = 6.0, 2 H). ^{13}C-NMR: 29.0; 31.3; 64.7; 101.8 (CN_2); 155.4.

Synthesis of α-Nitro-α-diazo Ketones **10**: Typical procedure according to [27], except that the mixture was cooled in an ice bath (at 0°) before a slow, dropwise addition of pyridine. The soln. was allowed to warm slowly to r.t. overnight, concentrated, and purified by FC (SiO_2; $CHCl_3$). Compounds **10c**,**e**,**f** have been previously reported [27].

1-Diazo-1-nitropropan-2-one (**10a**): 146 mg (83%). Pale yellow solid. M.p. 42°. IR (solid): 2163*s*, 1656*s*, 1497*s*, 1276*s*. ^{1}H-NMR: 2.66 (*s*, 3 H). ^{13}C-NMR: 29.2; 112.6 (CN_2); 184.4. (Note: this product readily sublimes *in vacuo*).

1-Diazo-1-nitropentan-2-one (**10b**): 112 mg (81%). Pale yellow solid. M.p. 36–37°. IR (solid): 2150*s*, 1664*s*, 1497*s*, 1310*s*. ^{1}H-NMR: 0.97 (*t*, *J* = 7.4, 2 H); 1.68 (*m*, 2 H); 2.96 (*t*, *J* = 7.3, 2 H). ^{13}C-NMR: 13.7; 17.2; 42.8; 112.3 (CN_2); 187.0.

1-Diazo-3-methyl-1-nitrobutan-2-one (**10d**): 259 mg (93%). Yellow oil. IR (film): 2170*s*, 2136*s*, 1666*s*, 1513*s*, 1313*s*. ^{1}H-NMR: 1.20 (*d*, *J* = 6.8, 6 H); 3.67 (*sept.*, *J* = 6.8, 1 H). ^{13}C-NMR: 18.2; 37.8; 191.2. HR-MS: 157.04927 ($C_5H_7N_3O_3^+$; calc. 157.04874).

1-(Adamant-1-yl)-2-diazo-2-nitroethanone (**10g**): 139 mg (93%). Yellow solid. M.p. 64–65°. IR (solid): 2164*s*, 1638*s*, 1495*s*, 1268*s*. ^{1}H-NMR: 1.77 (br., 6 H); 2.03 (br., 6 H); 2.10 (br., 3 H). ^{13}C-NMR: 28.1; 36.4; 36.6; 47.8; 115.0 (CN_2); 190.5.

tert-*Butyl* N-*(3-Diazo-1-benzyl-3-nitro-2-oxopropyl)carbamate* (**10h**): 114 mg (80%). Pale yellow solid. M.p. 128° (dec.). IR (solid): 2131*s*, 1684*s*, 1510*s*, 1309*s*. ^{1}H-NMR: 1.38 (*s*, 9 H); 2.75–2.81 (*m*, 1 H); 3.19–3.24 (*m*, 1 H); 5.04 (*d*, *J* = 8.3, 1 H); 5.54–5.59 (*m*, 1 H); 7.23–7.36 (*m*, 5 H). ^{13}C-NMR: 28.4; 37.7; 58.0; 80.7; 113.3; 127.6; 129.0; 129.5; 135.3; 155.3; 186.4.

Cyclopropanations with **10** *or* **17**. In a round-bottomed flask was added the appropriate catalyst (2 mol-% based on diazo compound). Freshly distilled alkene (5 equiv.) was added, then, the α-nitro-α-diazo carbonyl compound (0.50 mmol, 1 equiv.) in distilled CH_2Cl_2 (0.5 ml, 1.0M) was added *via* syringe ensuring a controlled rate of N_2 evolution. The soln. was stirred for 4 h, concentrated under reduced pressure, and purified by FC (SiO_2; hexanes/AcOEt 97:3) to yield the cyclopropanes.

Catalysts. $[Rh(OAc)_2]_2$ and $[Rh(cap)_2]_2$ were purchased from *Aldrich*, while $[Rh(CF_3CO_2)_2]_2$ and $[Rh(C_7H_{15}CO_2)_2]_2$ were purchased from *Strem Chemicals*. $[Rh(Me_3CO_2)_2]_2$ and $[Rh(Adaman)_2]_2$ were prepared according to known procedures [43][44]. Cyclopropanes **19**, **20a**,**b**,**d**,**g** have been previously reported [31].

Isopropyl cis- *and* trans-*1-Nitro-2-phenylcyclopropane-1-carboxylate* (**20c**): 97 mg (78%, *cis*/*trans* 25:75). Clear, colorless oil.

Data of trans-**20c**. IR (film): 1739*s*, 1545*s*, 1351*s*. ^{1}H-NMR: 0.82 (*d*, *J* = 6.3, 3 H); 1.02 (*d*, *J* = 6.3, 3 H); 2.18 (*dd*, *J* = 10.7, 6.6, 1 H); 2.44 (*dd*, *J* = 9.1, 6.6, 1 H); 3.76 (*t*, *J* = 9.7, 1 H); 4.81 (*sept.*, *J* = 6.3, 1 H); 7.20–7.33 (*m*, 5 H). ^{13}C-NMR: 20.6; 21.15; 21.21; 34.1; 70.8; 72.0; 128.4; 128.6; 128.7; 132.3; 161.5. HR-MS: 249.10065 ($C_{13}H_{15}NO_4^+$; calc. 249.10011).

Data of cis-**20c**: ^{1}H-NMR: 1.33 (*dd*, *J* = 6.3, 4.8, 6 H); 2.00 (*dd*, *J* = 9.9, 6.9, 1 H); 2.44 (*dd*, *J* = 9.1, 6.6, 1 H); 3.46 (*dd*, *J* = 9.8, 9.3, 1 H); 5.20 (*sept.*, *J* = 6.3, 1 H); 7.21–7.37 (*m*, 5 H). ^{13}C-NMR: 20.7; 21.7; 21.8; 33.6; 71.7; 73.0; 128.5; 128.8; 128.9; 131.7; 165.0. Anal. calc. for $C_{13}H_{15}NO_4$ (249.27): C 62.64, H 6.07, N 5.62; found: C 62.47, H 6.15, N 5.62.

cis- *and* trans-*1-(1-Nitro-2-phenylcyclopropyl)ethan-1-one* **(20e)**: 159 mg (77%, *cis*/*trans* 22:78). White solid.

Data of trans-**20e**: M.p. 67–69°. IR (solid): 1707*s*, 1528*s*, 1351*s*. ^{1}H-NMR: 2.09 (*s*, 3 H); 2.21 (*dd*, *J* = 10.6, 6.4, 1 H); 2.58 (*dd*, *J* = 9.0, 6.4, 1 H); 3.82 (*t*, *J* = 9.9, 1 H); 7.13–7.15 (*m*, 2 H); 7.29–7.32 (*m*, 3 H). ^{13}C-NMR: 20.3; 29.1; 37.2; 77.1; 128.5; 128.6; 129.0; 131.3; 193.7. HR-MS: 205.074398 ($C_{11}H_{11}NO_3^+$; calc. 205.073893).

Data of cis-**20e**: IR (film): 1707*s*, 1533*s*, 1357*s*. ^{1}H-NMR: 2.02 (*dd*, *J* = 9.8, 6.4, 1 H); 2.52 (*s*, 3 H); 2.73 (*dd*, *J* = 9.3, 6.5, 1 H); 3.56 (*t*, *J* = 9.5, 1 H); 7.19–7.21 (*m*, 2 H); 7.30–7.34 (*m*, 3 H). ^{13}C-NMR: 22.8; 27.8; 36.9; 84.3; 128.7; 128.87; 128.9; 131.6; 197.3. Anal. calc. for $C_{11}H_{11}NO_3$ (205.22): C 64.38, H 5.40, N 6.83; found: C 64.16, H 5.45, N 6.70.

cis- *and* trans-*1-(1-Nitro-2-phenylcyclopropyl)butan-1-one* (**20f**): 113 mg (74%, *cis*/*trans* 19:81). Clear, colorless oil, inseparable *cis*/*trans*-mixture. IR (film): 1716*s*, 1535*s*, 1349*s*.

Data of trans-**20f**: ^{1}H-NMR: 0.62 (*t*, *J* = 7.4, 3 H); 1.12–1.20 (*m*, 2 H); 1.35–1.39 (*m*, 2 H); 2.17 (*dd*, *J* = 10.6, 6.4, 1 H); 2.68 (*dd*, *J* = 6.4, 4.4, 1 H); 3.81 (*t*, *J* = 9.9, 1 H); 7.12–7.14 (*m*, 2 H); 7.26–7.33 (*m*, 3 H). ^{13}C-NMR: 13.4; 17.0; 20.1; 36.7; 43.5; 77.1; 128.6; 128.9; 131.4; 196.3. HR-MS 233.10524 ($C_{13}H_{15}NO_3^+$: 233.10519).

Data of cis-**20f**: ^{1}H-NMR: 0.96 (*t*, *J* = 7.4, 3 H); 1.65–1.75 (*m*, 1 H); 2.75–2.83 (*m*, 2 H); 2.90–3.05 (*m*, 1 H); 3.56 (*t*, *J* = 9.5, 1 H); 7.19–7.21 (*m*, 2 H); 7.26–7.33 (*m*, 3 H). ^{13}C-NMR: 13.7; 17.5; 22.5; 36.1; 41.6; 80.1; 128.7; 128.8; 129.2; 131.8; 199.5.

cis- *and* trans-*2,2-Dimethyl-1-(1-nitro-2-phenylcyclopropyl)propan-1-one* (**20h**): 148 mg (55%, *cis*/*trans* 80:20). White solid, inseparable *cis*/*trans*-mixture. M.p. 48–50°. IR (solid): 1705*s*, 1539*s*.

Data of trans-**20h**: ^{1}H-NMR: 0.82 (*s*, 9 H); 1.98 (*dd*, *J* = 10.7, 6.5, 1 H); 2.54 (*dd*, *J* = 9.2, 6.5, 1 H); 3.86 (*t*, *J* = 9.3, 1 H); 7.09–7.12 (*m*, 1 H); 7.39–7.24 (*m*, 4 H). ^{13}C-NMR: 20.2; 27.2; 34.8; 44.9; 76.6; 128.5; 128.6; 128.9; 131.7; 202.4.

Data of cis-**20h**: IR (film): 1705*s*, 1533*s*. ^{1}H-NMR: 1.31 (*s*, 9 H); 1.71 (*dd*, *J* = 9.8, 6.8, 1 H); 2.76 (*dd*, *J* = 9.4, 6.8, 1 H); 3.55 (*t*, *J* = 9.6, 1 H); 7.09–7.12 (*m*, 1 H); 7.24–7.39 (*m*, 4 H). ^{13}C-NMR: 20.2; 28.2; 31.7; 46.2; 76.7; 128.5; 128.7; 129.0; 131.8; 203.2. HR-MS: 247.121697 ($C_{14}H_{17}NO_3^+$; calc. 247.120844). Anal. calc. for $C_{14}H_{17}NO_3$ (247.30): C 68.00, H 6.93, N 5.66; found: C 68.27, H 7.06, N 5.70.

Ethyl 2-Methyl-1-nitro-2-phenylcyclopropane-1-carboxylate (**22a**): 118 mg (95%). White solid, as a cyclopropane/isoxazoline oxide mixture (78:28) after chromatography.

Data of cis-**22a**: M.p. 54–55°. IR (film): 1736*s*, 1543*s*. ^{1}H-NMR: 0.89 (*t*, *J* = 7.1, 3 H); 1.54 (*s*, 3 H); 2.15 (*d*, *J* = 6.8, 1 H); 2.42 (*d*, *J* = 6.8, 1 H); 3.89–3.95 (*m*, 2 H); 7.26–7.35 (*m*, 5 H). ^{13}C-NMR: 13.7; 25.1; 26.5; 39.4; 62.7; 76.4; 127.9; 128.0; 128.8; 139.3; 163.8. HR-MS 250.106823 ($C_{13}H_{15}NO_4^+$: calc. 250.107933).

Data of 4,5-Dihydro-5-methyl-5-phenylisoxazole-3-carboxylic Acid Ethyl Ester 2-Oxide: IR (film): 1723*s*, 1606*s*. ^{1}H-NMR: 1.32 (*t*, *J* = 7.1, 3 H); 1.82 (*s*, 3 H); 3.57 (*m*, 2 H); 4.29 (*q*, *J* = 7.2, 2 H); 7.45–7.33 (*m*, 5 H). ^{13}C-NMR: 14.4; 28.3; 44.5; 62.0; 82.9; 109.1; 124.3; 128.4; 129.1; 143.1; 159.2.

Ethyl 1-Nitro-2,2-diphenylcyclopropane-1-carboxylate (**22b**): Observed in the crude reaction mixture. ^{1}H-NMR: 0.98 (*t*, *J* = 7.2, 3 H); 2.67 (*d*, *J* = 6.9, 1 H); 3.01 (*d*, *J* = 6.9, 1 H); 3.98–4.08 (*m*, 2 H); 7.31–7.45 (*m*, 10 H). After FC (SiO_2), *4,5-dihydro-5,5-diphenyl-isoxazole-3-carboxylic acid ethyl ester 2-oxide* was obtained (64 mg, 60%). Pale yellow solid. M.p. 101–103°. IR (solid): 1731*s*, 1620*s*. ^{1}H-NMR: 1.33 (*dt*, *J* = 7.1, 0.6, 3 H); 4.04 (*s*, 2 H); 4.30 (*dq*, *J* = 7.1, 0.6, 2 H); 7.31–7.45 (*m*, 10 H). ^{13}C-NMR: 14.4; 43.8; 62.2; 86.0; 109.0; 125.9; 128.7; 129.0; 141.6; 159.1. HR-MS: 312.123909 ($C_{18}H_{17}NO_4^+$; calc. 312.123583). Anal. calc. for $C_{18}H_{17}NO_4$ (311.33): C 69.44, H 5.50, N 4.50; found: C 69.63, H 5.53, N 4.37.

Ethyl exo- *and* endo-*1,1a,6,6a-Tetrahydro-1-nitrocyclopropa[a]indene-1-carboxylate* (**22c**): 120 mg (84%, *exo*/*endo* 97:3). White solid.

Data of exo-**22c**: M.p. 57–58°. IR (film): 1739*s*, 1539*s*, 1338*s*. ^{1}H-NMR: 0.82 (*dt*, *J* = 7.1, 0.26, 3 H); 3.12 (*ddd*, *J* = 7.3, 6.2, 0.9, 1 H); 3.40 (*dd*, *J* = 18.0, 6.1, 1 H); 3.49 (*d*, *J* = 18.0, 1 H); 3.82 (*d*, *J* = 7.4, 1 H); 3.85–3.92 (*m*, 2 H); 7.15–7.26 (*m*, 3 H); 7.42–7.44 (*m*, 1 H). ^{13}C-NMR: 13.5; 34.4; 42.0; 62.3; 72.9; 125.1; 126.0; 127.5; 128.3; 137.9; 142.0; 160.5. HR-MS: 247.084385 ($C_{13}H_{13}NO_4^+$; calc. 247.084458). Anal. calc. for $C_{13}H_{13}NO_4$ (247.08): C 63.15, H 5.30, N 5.67; found: C 63.11, H 5.30, N 5.65.

Data of endo-**22c**: ^{1}H-NMR: 1.31 (*t*, *J* = 7.1, 3 H); 2.94 (*dt*, *J* = 7.1, 1.6, 1 H); 4.33 (*q*, *J* = 7.2, 2 H); 7.21–7.49 (*m*, 4 H).

Ethyl cis- *and* trans-*2-butyl-1-nitrocyclopropane-1-carboxylate* (**22d**): 38 mg (40%, *cis*/*trans* 40:60). Clear, colorless oil, inseparable *cis*/*trans*-mixture. IR (film): 1742*s*, 1545*s*.

Data of trans-**22d**: ^{1}H-NMR: 0.88 (*t*, *J* = 7.3, 3 H); 1.14–1.53 (*m*, 10 H); 1.63–1.70 (*m*, 2 H); 1.81–1.88 (*m*, 2 H); 2.37–2.44 (*m*, 2 H); 4.32 (*q*, *J* = 7.2, 2 H). ^{13}C-NMR: 14.2; 22.3; 22.6; 23.3; 27.7; 28.1; 30.6; 62.9; 70.7; 163.8.

Data of cis-**22d**: ^{1}H-NMR: 0.89 (*t*, *J* = 7.3, 3 H); 1.14–1.53 (*m*, 10 H); 2.08–2.14 (*m*, 2 H); 4.29 (*m*, 2 H). ^{13}C-NMR: 14.0; 14.1; 22.3; 22.4; 23.3; 29.5; 30.8; 63.1; 71.7; 163.8. HR-MS: 216.123199 ($C_{10}H_{17}NO_4^+$; calc. 216.123583). Anal. calc. for $C_{10}H_{17}NO_4$ (215.24): C 55.80, H 7.96, N 6.51; found: C 55.79, H 8.08, N 6.41.

Ethyl cis- *and* trans-*2-bromo-2-methyl-1-nitrocyclopropane-1-carboxylate* (**22e**): 62 mg (50%, *cis*/*trans* 20:80). Clear, colorless oil, inseparable *cis*/*trans*-mixture. IR (film): 1745*s*, 1552*s*.

Data of trans-**22e**: ^{1}H-NMR: 1.34 (*t*, *J* = 7.1, 3 H); 1.94 (*s*, 3 H); 2.21 (*d*, *J* = 8.6, 1 H); 2.37 (*d*, *J* = 8.6, 1 H); 4.35 (*q*, *J* = 7.1, 2 H). ^{13}C-NMR: 14.2; 27.0; 30.6; 34.4; 63.9; 74.5; 162.1.

Data of cis-**22e**: ^{1}H-NMR: 1.32 (*t*, *J* = 7.2, 3 H); 2.06 (*s*, 3 H); 2.12 (*d*, *J* = 8.7, 1 H); 2.49 (*d*, *J* = 8.7, 1 H); 4.30 (*q*, *J* = 7.1, 2 H). ^{13}C-NMR: 14.1; 24.9; 31.4; 36.2; 63.8; 76.9; 163.0. Anal. calc. for $C_7H_{10}BrNO_4$ (252.07): C 33.35, H 4.00, N 5.56; found: C 33.39, H 4.04, N 5.48.

Ethyl cis- *and* trans-*2-bromo-1-nitro-2-phenylcyclopropane-1-carboxylate* (**22f**): 160 mg (77%, *cis*/*trans* 75:25). Pale yellow solid.

Data of trans-**22f**: Clear, colorless oil. IR (film): 1746*s*, 1554*s*. ^{1}H-NMR: 1.44 (*t*, *J* = 7.2, 3 H); 2.59 (*d*, *J* = 8.7, 1 H); 3.03 (*d*, *J* = 8.8, 1 H); 4.48 (*q*, *J* = 7.2, 2 H); 7.34–7.39 (*m*, 3 H); 7.45–7.48 (*m*, 2 H). ^{13}C-NMR: 14.2; 28.9; 39.7; 63.9; 74.5; 128.8; 129.1; 130.0; 134.2; 161.6.

Data of cis-**22f**: Yellow solid. M.p. 79–80°. IR (film): 1732*s*, 1548*s*. ^{1}H-NMR (300 MHz): 0.93 (*t*, *J* = 7.1, 3 H); 2.75 (*d*, *J* = 8.7, 1 H); 2.83 (*d*, *J* = 8.7, 1 H); 3.95–3.99 (*m*, 2 H); 7.35–7.37 (*m*, 3 H); 7.44–7.46 (*m*, 2 H). ^{13}C-NMR (75 MHz): 13.6; 29.5; 39.4; 63.5; 75.1; 128.6; 129.0; 129.6; 137.2; 161.7. HR-MS: 312.995537

($C_{12}H_{12}BrNO_4^+$; calc. 312.994969). Anal. calc. for $C_{12}H_{12}BrNO_4$ (314.14): C 45.88, H 3.85, N 4.46; found: C 45.99, H 3.86, N 4.51.

Synthesis of α-Alkoxy-α-nitro Carbonyl Compounds. Typical Procedure. To a mixture of rhodium(II) acetate (8.8 mg 5.0 mol-%) and the alcohol (2.5 mmol, 5 equiv.) was added dropwise a soln. of the α-nitro-α-diazo ester (0.5 mmol, 1 equiv.) in dry CH_2Cl_2 (0.50 ml, 1.0M). The mixture was stirred for 2–4 h at 20°, concentrated under reduced pressure, and purified by FC (SiO_2; hexanes/AcOEt 95:5).

Ethyl 2-(Allyloxy)-2-nitroacetate (**23a**): 74 mg (84%). Clear, colorless oil. IR (film): 1760*s*, 1575*s*. ^{1}H-NMR: 1.33 (*t*, *J* = 7.1, 3 H); 4.21–4.26 (*m*, 1 H); 4.33 (*q*, *J* = 7.1, 2 H); 4.48–4.53 (*m*, 1 H); 5.38–5.44 (*m*, 2 H); 5.60 (*s*, 1 H); 5.89–5.98 (*m*, 1 H). ^{13}C-NMR: 14.0; 63.8; 73.9; 103.3; 121.8; 131.0; 161.7.

Ethyl 2-(Benzyloxy)-2-nitroacetate (**23b**): 97 mg (99%). Clear, colorless oil. IR (film): 1760*s*, 1575*s*. ^{1}H-NMR: 1.31 (*t*, *J* = 7.1, 3 H); 4.31 (*q*, *J* = 7.1, 2 H); 4.73 (*d*, *J* = 11.6, 1 H); 5.06 (*d*, *J* = 11.6, 1 H); 5.59 (*s*, 1 H); 7.38–7.42 (*m*, 5 H). ^{13}C-NMR: 14.0; 63.8; 74.6; 103.2; 129.0; 129.1; 129.4; 134.0; 161.6. Anal. calc. for $C_{11}H_{13}NO_5$ (239.04): C 55.23, H 5.48, N 5.86; found: C 55.25, H 5.52, N 5.88.

*Ethyl 2-(*tert-*Butoxy)-2-nitroacetate* (**23c**): 38 mg (45%). Clear, colorless oil. IR (film): 1760*s*, 1575*s*. ^{1}H-NMR: 1.30 (*t*, *J* = 7.2, 3 H); 1.32 (*s*, 9 H); 4.29 (*dq*, *J* = 1.3, 7.2, 2 H); 5.73 (*s*, 1 H). ^{13}C-NMR: 14.0; 27.5; 63.6; 81.6; 100.0; 163.1.

Ethyl 2-(Cyclopropylmethoxy)-2-nitroacetate (**23d**): 83 mg (87%). Clear, colorless oil. IR (film): 1760*s*, 1574*s*. ^{1}H-NMR: 0.28–0.35 (*m*, 2 H); 0.62–0.68 (*m*, 2 H); 1.15–1.19 (*m*, 1 H); 1.33 (*t*, *J* = 7.1, 3 H); 3.65–3.70 (*m*, 2 H); 4.33 (*q*, *J* = 7.1, 2 H); 5.68 (*s*, 1 H). ^{13}C-NMR: 3.3; 3.9; 9.8; 14.0; 63.8; 78.3; 104.2; 161.9.

*Methyl (*2R*)-3-[(Ethoxycarbonyl)(nitro)methoxy]-2-methylpropanoate* (**23e**): 125 mg (74%) as a *ca.* 50:50 mixture of diastereoisomers. Clear, colorless oil. IR (film): 1742*s*, 1576*s*, 1463*s*. ^{1}H-NMR: 1.25 (*d*, *J* = 7.2, 3 H); 1.30 (*d*, *J* = 7.2, 3 H); 1.344 (*t*, *J* = 7.1, 3 H); 1.338 (*t*, *J* = 7.1, 3 H); 2.87–2.98 (*m*, 1 H); 3.74 (*s*, 3 H); 3.87–3.99 (*m*, 1 H); 4.02–4.06 (*m*, 0.5 H); 4.16–4.21 (*m*, 0.5 H); 4.32–4.36 (*m*, 2 H); 5.624 (*s*, 1 H); 5.629 (*s*, 1 H). ^{13}C-NMR: 13.8; 14.0; 39.8; 40.0; 52.2; 63.70; 63.74; 74.7; 74.9; 104.7; 105.0; 161.4; 161.5; 173.9; 174.3.

Benzyl 2-(Allyloxy)-2-nitroacetate (**23f**): 92 mg (92%). Clear, colorless oil. IR (film): 1760*s*, 1573*s*. ^{1}H-NMR: 4.21–4.26 (*m*, 1 H); 4.48–4.53 (*m*, 1 H); 5.29 (*s*, 2 H); 5.37–5.42 (*m*, 2 H); 5.64 (*s*, 1 H); 5.87–5.97 (*m*, 1 H); 7.33–7.41 (*m*, 5 H). ^{13}C-NMR: 69.1; 73.9; 103.1; 121.7; 128.6; 128.9; 129.1; 130.9; 134.1; 161.6.

Benzyl 2-(Benzyloxy)-2-nitroacetate (**23g**): 101 mg (84%). Clear, colorless oil. IR (film): 1761*s*, 1574*s*. ^{1}H-NMR: 4.73 (*d*, *J* = 11.6, 1 H); 5.06 (*d*, *J* = 11.6, 1 H); 5.26 (*s*, 2 H); 5.62 (*s*, 1 H); 7.31–7.41 (*m*, 10 H). ^{13}C-NMR: 69.0; 74.7; 103.2; 128.5; 128.7; 128.8; 128.9; 129.0; 129.3; 134.0; 134.1; 161.5.

*Benzyl 2-[(1*R*,2*S*,5*R*)-Menthyloxy]-2-nitroacetate* (**23h**): 110 mg (79%) as 55:45 mixture of diastereoisomers. Clear, colorless oil. M.p. 40–42°. IR (film): 1745*s*, 1571*s*. ^{1}H-NMR: 0.77 (*d*, *J* = 6.9, 6 H); 0.86 (*d*, *J* = 7.0, 6 H); 0.85–0.94 (*m*, 20 H); 1.00–1.14 (*m*, 2 H); 1.26–1.49 (*m*, 6 H); 1.60–1.72 (*m*, 6 H); 1.90–2.12 (*m*, 4 H); 2.43–2.47 (*m*, 1 H); 3.50–3.58 (*m*, 2 H); 5.22–5.32 (*m*, 4 H); 5.64 (*s*, 1 H); 5.78 (*s*, 1 H); 7.31–7.41 (*m*, 10 H). ^{13}C-NMR: 15.9; 16.0; 20.9; 21.2; 22.2; 22.3; 23.0; 23.1; 25.4; 25.5; 31.6; 31.8; 34.0; 34.1; 39.3; 40.4; 40.5; 47.8; 48.1; 68.8; 69.0; 82.4; 87.3; 102.0; 105.4; 128.5; 128.7; 128.9; 129.0; 129.1; 134.2; 134.3; 162.26; 162.31. Anal. calc. for $C_{19}H_{27}NO_5$ (349.42): C 65.31, H 7.79, N 4.01; found: C 65.61, H 8.05, N 3.95.

1-(Allyloxy)-1-nitro-2-phenylethan-2-one (**23i**): 86 mg (78%). Pale yellow oil. IR (film): 1700*s*, 1574*s*. ^{1}H-NMR: 4.33–4.38 (*m*, 1 H); 4.58–4.63 (*m*, 1 H); 5.40–5.45 (*m*, 2 H); 5.94–6.04 (*m*, 1 H); 6.20 (*s*, 1 H); 7.48–7.52 (*m*, 2 H); 7.63–7.67 (*m*, 1 H); 7.97–7.99 (*m*, 2 H). ^{13}C-NMR: 74.3; 106.4; 121.9; 129.2; 129.7; 131.0; 132.6; 135.1; 185.9. Anal. calc. for $C_{11}H_{11}NO_4$ (221.22): C 59.73, H 5.01, N 6.33; found: C 59.45, H 4.99, N 6.25.

Ethyl 2-(Isopropoxy)-2-nitroacetate (**23j**): 413 mg (72%). Clear, colorless oil. IR (film): 1761*s*, 1575*s*. ^{1}H-NMR: 1.25–1.38 (*m*, 9 H); 3.99 (*sept.*, *J* = 7.1, 1 H) 4.32 (*q*, *J* = 7.1, 2 H); 5.61 (*s*, 1 H). ^{13}C-NMR: 14.3; 21.6; 22.7; 64.0; 76.9; 103.8; 162.7. Anal. calc. for $C_7H_{13}NO_5$ (191.19): C 43.98, H 6.85, N 7.33; found: C 43.99, H 6.82, N 7.24.

X-Ray Crystal-Structure Analyses of **17a** *and the Methyl Ester Derivative of* **22c**. The intensities of both crystals were collected on a *Nonius CAD-4* diffractometer with CuK_α radiation (λ = 1.54056 Å) and $\omega/2\theta$ scan. The structures were solved by direct methods and refined on F^2(SHELXL96). H-atoms were treated as riding.

Crystals of **17a** were grown from a $CHCl_3$ soln. They were orthorhombic, $C_{1.5}H_{1.5}N_{1.5}O_2$, M_r 72.542 g mol^{-1}, crystal size 0.49 × 0.48 × 0.38 mm, space group $P2_12_12_1$, a = 13.322(2) Å, b = 5.949(2) Å, c = 7.364(2) Å, V = 583.6(3) Å^3, Z = 8; D_x = 1.6512 Mg m^{-3}, No. of reflections measured = 4240, observed = 611 ($I > 2\sigma(I)$), intensity decay = 7.3%, θ_{max} = 69.84°, No. of refined parameters = 63, R factor = 0.0406, wR = 0.1016, S = 1.052, diff. density$_{max}$ = 0.268 e Å^{-3}, diff. density$_{min}$ = −0.154 e Å^{-3}.

Crystals of *methyl* exo-*1,1a,6,6a-tetrahydro-1-nitrocyclopropa[*a*]indene-1-carboxylate* were grown from an AcOEt/hexanes soln. They were monoclinic, $C_{12}H_{11}NO_4$, M_r 233.218 g mol^{-1}, crystal size 0.20 × 0.14 × 0.05 mm, space group $P2_12_12_1$, a = 10.026(3) Å, b = 14.221(5) Å, c = 8.566(3) Å, V = 1136.4(7) Å^3, Z = 4; D_x = 1.3631 Mg

m^{-3}, No. of reflections measured = 16427, observed = 2159 ($I > 2\sigma(I)$), intensity decay = 14.0%, $\theta_{max} = 69.82°$, No. of refined parameters = 156, R factor = 0.0387, $wR = 0.0816$, $S = 0.726$, diff. density$_{max}$ = 0.160 e Å^{-3}, diff. density$_{min}$ = −0.146 e Å^{-3}.

Supplementary crystallographic data has been deposited with the *Cambridge Crystallographic Data Centre* as deposition Nos.: CCDC-189718 (**17a**) and -189717 (methyl *exo*-1,1a,6,6a-tetrahydro-1-nitrocyclopropa[*a*]indene-1-carboxylate). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: + 44(1223)336033; e-mail: deposit@ccdc.com.ac.uk).

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