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Factors in Molecular Structure to Activate Nitro Compounds for Organic Transformations

Den-Nan Horng,[a,*] Keh-Loong Chen[b] and Jih Ru Hwu[b]

[a]*Department of Physics and Chemistry, Chinese Military Academy, P.O. Box 90602-6, Feng-shan, Taiwan, ROC*
[b]*Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, ROC*

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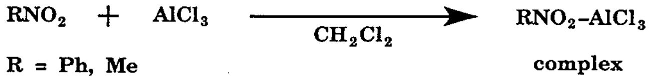
Abstract—Activation of nitro compounds was accomplished by introduction of angle strain, γ,δ-unsaturation, or a γ-silyl group. Results from a systematic study indicate that coexistence of two or more of these factors in aliphatic nitro compounds allowed transformations to take place under ambient conditions upon catalysis with $AlCl_3$, $TiCl_4$, $BF_3\cdot OEt_2$, or $SnCl_4$. Consequently, structurally modified nitro starting materials led to products in the class of nitroalkyl cyclopentadiene, cyclohydroxamic ester, and chlorohydroxamic acid. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Lewis acids can coordinate with nitro compounds to form complexes (see Scheme 1).[1] These nitro compounds can be recovered after the Lewis acid is removed. On the other hand, introduction of certain moieties (such as –OH, C=O, –SR, etc.) to organic nitro compounds may allow functional group transformations to take place.[2–6] We decided to search for structural factors that can activate aliphatic nitro compounds under acidic conditions. After the structure is modified, the nitro compounds would undergo transformations smoothly upon Lewis acid catalysis.



$$\underset{R\ =\ Ph,\ Me}{RNO_2} + AlCl_3 \xrightarrow[CH_2Cl_2]{} \underset{\text{complex}}{RNO_2\text{-}AlCl_3}$$

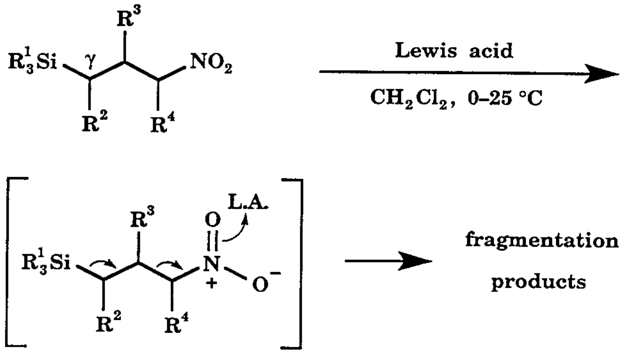
Scheme 1.

Reactivity of the commonly used Lewis acids follows the order $AlCl_3 > TiCl_4 > BF_3\cdot OEt_2 > SnCl_4$.[7] We applied these acids to structurally 'activated' nitro compounds and intended to realize the consequent transformations. Herein, we report our findings on three structural factors that can enhance the reactivity of aliphatic nitro compounds. They include buildup of angle strain, existence of γ,δ-unsaturation, and placement of a γ-silyl group.

Introduction of a silyl group into aliphatic nitro compounds is of particular significance. Its attachment to the hydrocarbon skeleton often does not alter polarity of organic compounds; yet silicon may exert an electronic effect on ionic and radical intermediates generated in reactions involving organosilanes as the substrates.[8] As a consequence, we found some transformations occurring to these silicon-containing nitro compounds based on the strategy shown in Scheme 2. The intriguing conversion of activated nitro compound **12** to hydroxamic acid derivatives **13** and **14**, as shown in Scheme 6, is also unprecedented.

Results and Discussion

To explore a way to increase the reactivity of nitro compounds, we introduced different moieties onto the skeleton of nitro compounds. First, we found that nitro compound **1**[9] bearing a β-phenyl group remained intact upon treatment



Scheme 2.

Keywords: nitro compounds; fragmentation reaction; Lewis acids.

* Corresponding author. E-mail: horng@ms31.url.com.tw

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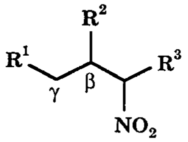
Table 1. Reaction of nitro compounds with a Lewis acid in dichloromethane

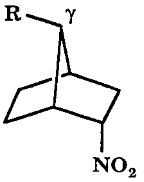
Entry	Nitro compound	Lewis acid	Temperature (°C)	Reaction time	Result (yield)
1	**1**	$AlCl_3$	0–25	72 h	Intact
2	**2**	$AlCl_3$	0–25	2.0 h	Styrene (85%)
3	**3**	$AlCl_3$	25	72 h	Intact
4	**3**	$TiCl_4$	25	72 h	Intact
5	**3**	$BF_3 \cdot OEt_2$	25	72 h	Intact
6	**3**	$SnCl_4$	25	72 h	Intact
7	**4**	$AlCl_3$	25	12 h	Fragmentation[a]
8	**5**	$AlCl_3$	25	72 h	Intact
9	**6**	$AlCl_3$	25	12 h	**7** (23%)
10	**6**	$TiCl_4$	25	10 min	**7** (42%)
11	**6**	$SnCl_4$	25	72 h	Epimerization (23%)
12	**8**	$AlCl_3$	0	5.0 min	**10** (99%)
13	**8**	$SnCl_4$	25	72 h	Epimerization (18%)
14	**9**	$AlCl_3$	0	5.0 min	**10** (98%)
15	**9**	$SnCl_4$	25	72 h	Epimerization (17%)
16	**12**	$AlCl_3$	0	5.0 min	**13** (48%)+**14** (23%)
17	**12**	$SnCl_4$	25	12 h	**13** (78%)
18	**15**	$AlCl_3$	25	12 h	**16** (72%)+$(Et_3Si)_2O$ (94%)
19	**15**	$TiCl_4$	25	12 h	**16** (66%)+$(Et_3Si)_2O$ (79%)
20	**15**	$BF_3 \cdot OEt_2$	25	12 h	**16** (58%)+$(Et_3Si)_2O$ (77%)
21	**15**	$SnCl_4$	25	12 h	**16** (67%)+$(Et_3Si)_2O$ (86%)

[a] An inseparable mixture was obtained.

with $AlCl_3$ in dichloromethane at 0–25°C for 72 h (see entry 1 in Table 1). These results indicate that attachment of a phenyl group at the β position does not significantly increase the reactivity of nitro compounds.



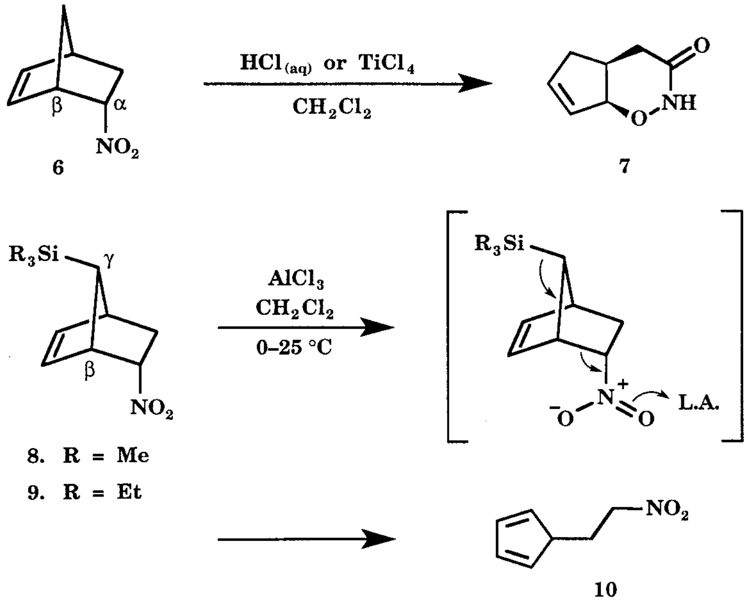
1. $R^1 = R^3 = H, R^2 = Ph$
2. $R^1 = SiMe_3, R^2 = Ph, R^3 = H$
3. $R^1 = SiMe_3, R^2 + R^3 = (CH_2)_4$



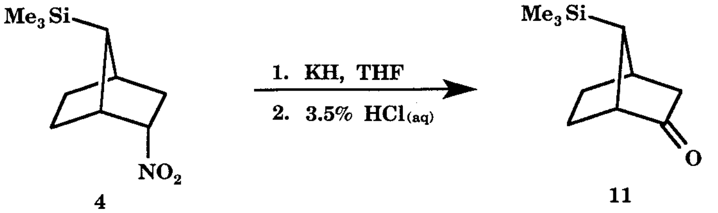
4. $R = SiMe_3$
5. $R = H$

Second, we added a trimethylsilyl group at the γ position and a phenyl group at the β position as shown in compound **2**. Under the same reaction conditions, complete fragmentation occurred to **2** to give styrene in 85% yield within 2.0 h (see entry 2 in Table 1). Similarly, γ-silyl nitronorbornane **4** was decomposed to give an inseparable mixture upon treatment with $AlCl_3$ (entry 7), yet non-silylated nitronorbornane **5**[10] was found intact (entry 8). Thus, introduction of a γ-silyl group into nitro compounds could increase their reactivity towards a Lewis acid although it may not be the only factor responsible for a fragmentation to take place.

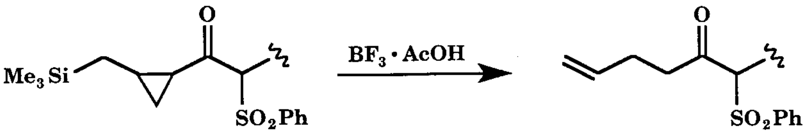
Third, we found that *cis*- and *trans*-nitrocyclohexanes **3** were intact towards all four Lewis acids (see entries 3–6 in Table 1). These γ-silyl nitro compounds do not possess a



Scheme 3.



Scheme 4.



Scheme 5.

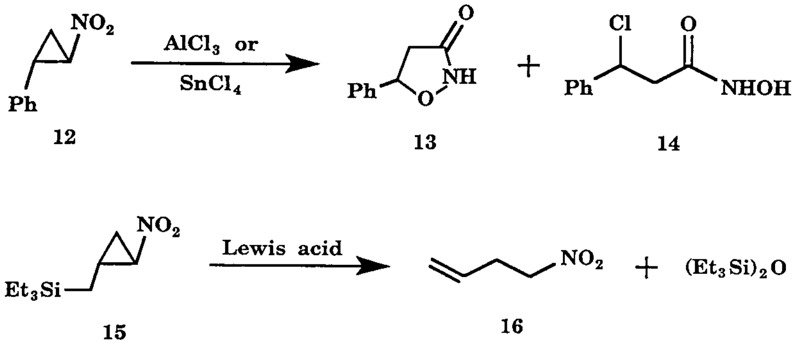
β-phenyl group (cf. **2**), nor angle strain (cf. **4**). In comparison with our observations on **2** and **4**, we believe that these two structural factors also contribute to the activity of aliphatic nitro compounds under acidic conditions.

Ranganathan et al.[11] reported that the sodium salt of **6**[12] goes through an abnormal Nef reaction to give cyclic hydroxamic ester **7** (Scheme 3). We found that the same conversion can be accomplished in 42% yield by using $TiCl_4$ (see entry 10 in Table 1). Compound **6**, however, was decomposed to give a mixture containing **7** (23%) upon exposure to a stronger Lewis acid $AlCl_3$ (entry 9). It was, however, epimerized at the α carbon by a weaker Lewis acid $SnCl_4$ (entry 11). Epimerization also occurred to the corresponding silylated dihydronorbornene nitro compounds **8** and **9** upon treatment with a weaker Lewis acid $SnCl_4$ (entries 13 and 15).

Silicon can exert α- and β-effects, which allow reactions to take place in a promoted or directed manner.[8,13] Reactions involving the γ-effect of silicon, however, are limited; silicon-promoted Nef reaction shown in Scheme 4 represents a prominent example.[10] The conversion of γ-silyl bicyclic nitro compound **4** to the corresponding ketone **11** can be accomplished in 91% yield by use of KH in THF followed by 3.5% of aqueous HCl. In comparison with compounds **4** and **6**, nitro compounds **8** and **9** possess all of the three structural features: a γ-silyl group, angle strain, and a vinyl moiety attached at the β position. The silyl groups anti to the nitro groups in **8** and **9** offered an ideal alignment for a stereoelectronic effect. We found that these silyl nitronorbornenes readily gave the ring-opening product **10** in excellent yields by loss of a silyl group upon treatment with $AlCl_3$ at 0°C (entries 12 and 14). The efficiency was independent upon the bulk of the silyl group therein including the Me_3Si group in **8** and the Et_3Si group in **9**. These reactions may go through a concerted pathway.

The ^1H NMR spectrum of the product **10** showed four vinylic protons. Therefore we assigned the nitroalkyl substituent therein attached to the sp^3 carbon of a cyclopentadiene nucleus. During the fragmentation process, the two C–C double bonds did not scramble in the five-membered nucleus. We believe that it is due to the mild conditions applied to the reaction.

Fujita et al.[14] reported a method for ring opening of γ-silyl cyclopropyl ketones by Lewis acids (see Scheme 5). We introduced a β-phenyl or a γ-silyl group into a nitrocyclopropane and then explored their reactivity towards Lewis acids (see Scheme 6). Upon treatment with $AlCl_3$ at 0°C, phenylcyclopropane **12**[15] gave a mixture of cyclohydroxamic ester **13**[16] (48% yield) and chlorohydroxamic acid **14**[17] (23% yield, entry 16 in Table 1). Replacement of $AlCl_3$ with a weaker Lewis acid $SnCl_4$ afforded an appealing yield of **13** (78%, entry 17). Both of hydroxamic derivatives **13** and **14** came from Lewis acid induced opening of a nitrocyclopropyl ring. Participation of the nitro group in an intramolecular cyclization led **12** to **13**. The unexpected by-product **14** was generated from an intermolecular chloride ion transfer from $AlCl_3$ to the ring-opening



Scheme 6.

intermediate. In its mass spectrum, two sets of peaks at 183/181 and 127/125 exhibited a ratio of 1:3. These results clearly indicate the presence of a chlorine atom in this by-product.

Furthermore, we found that silylcyclopropane **15** underwent fragmentation upon treatment with all four Lewis acids. Hexaethyldisiloxane was isolated in 77–94% yields and 4-nitro-1-butene (**16**)[18,19] in 58–72% yields (entries 18–21 in Table 1).

Conclusions

Our results from a systematic study indicate that aliphatic nitro compounds can be activated by having two or more of the following structural features: angle strain, γ, δ-unsaturation, and a γ-silyl group. Upon treatment with an appropriate Lewis acid, these activated nitro compounds often underwent fragmentation to give products of various classes.

Experimental

General procedure

All reactions were carried out in oven-dried glassware (120°C) under an atmosphere of nitrogen. Tetrahydrofuran (reagent grade) from Mallinckrodt was dried by distillation from sodium and benzophenone. Dichloromethane, ethyl acetate, and hexanes from Mallinckrodt Chemical Co. were dried and distilled from CaH_2. Dimethyl sulfoxide from Aldrich was dried and distilled from CaH_2 and stored in serum-capped bottles under argon over molecular sieves 4A. *trans*-β-Nitrostyrene, triethylsilyl chloride, (trimethylsilyl)methylmagnesium chloride, and trimethylsulfoxonium iodide were purchased from Aldrich Chemical Co. Aluminum chloride, boron trifluoride diethyl etherate, cyclopentadiene, sodium, sodium hydride, tin(IV) chloride, and titanium(IV) chloride were purchased from Merck Inc. 2-*endo*-Nitrobicyclo[2.2.1]heptane,[10] 2-*endo*-nitrobicyclo-[2.2.1]-hept-5-ene,[12] nitroethylene,[12] *trans*-1-nitro-2-phenylcyclopropane,[15] 1-nitro-2-phenylpropane,[9] *trans*-1-nitro-3-(triethylsilyl)-1-propene,[20] 2-[(trimethylsilyl)methyl]-1-nitrocyclohexane,[10] 7-*anti*-(trimethylsilyl)-2-nitrobicyclo[2.2.1]-heptane,[10] and 7-*syn*-(trimethylsilyl)-2-*endo*-nitrobicyclo-[2.2.1]hept-5-ene[12] were prepared by literature methods. The final products were purified as stated; their purity was >99.5% as determined by GC.

Melting points were obtained with a Büchi 535 melting point apparatus. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument equipped with a 25 m cross-linked methyl silicone gum capillary column (0.32 mm i.d.). Nitrogen gas was used as a carrier gas and the flow rate was kept constant at 14.0 mL/min. The retention time t_R was measured under the following conditions: injector temperature 260°C, the initial temperature for column 70°C, duration 2.00 min, increment rate 10°C/min, and the final temperature for column 250°C. Analytical thin layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254), purchased from Merck Inc. Visualization of spots on TLC plates was done by use of UV light. Mixtures of ethyl acetate and hexanes were used as eluants. Purification by radial thin-layer chromatography were performed on a Model 7924T Chromatotron from Harrison Research, Palo Alto. The plates (1, 2, and 4 mm thickness) were coated with EM Reagents silica gel 60 PF_{254} containing gypsum.

Proton NMR spectra were obtained on a Varian Unity-400 (400 MHz) spectrometer by use of chloroform-*d* as solvent and tetramethylsilane as internal standard. Carbon-13 NMR spectra were obtained on a Varian Unity-400 (100 MHz) spectrometer by use of chloroform-*d* as solvent. Carbon-13 chemical shifts are referenced to the center of the $CDCl_3$ triplet (δ 77.0 ppm). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *J*, coupling constant (hertz). Infrared (IR) spectra were measured on a Bomem Michelson Series FT-IR spectrometer. The wave numbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak. Low resolution mass spectral analyses were performed on a Hewlett-Packard 5890 Series II instrument equipped with a Hewlett-Packard 5971A Mass Selective Detector and a capillary HP-1 column. High-resolution mass spectra were obtained by means of a JEOL JMS-HX110 mass spectrometer.

1-Nitro-2-phenyl-3-(trimethylsilyl)propane (2). A solution of *trans*-β-nitrostyrene (1.12 g, 7.49 mmol, 1.0 equiv.) in THF (5.0 mL) was added dropwise to a solution of (trimethylsilyl)methylmagnesium chloride (1.00 M in ether, 9.74 mL, 9.74 mmol, 1.30 equiv.) in THF (3.0 mL) at −20°C. After the solution was stirred at the same temperature for 15 min, ice–water (15 mL) and ether (150 mL) were added into the reaction flask to quench the reaction. This solution was neutralized with 3.5% aqueous HCl (12 mL). At the end-point of acidification, the aqueous layer became colorless. The ether layer was washed with saturated aqueous $NaHCO_3$ (25 mL×2) and the aqueous layer was back extracted with Et_2O (15 mL×5). The combined etheral solutions were washed with saturated aqueous NaCl (25 mL), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure to give a light green oil. The oil was purified by use of a Chromatotron (4 mm plate, 1% EtOAc in hexanes as eluant) to give pure **2** (1.65 g, 6.97 mmol) as a light green oil in 93% yield: GC t_R 14.74 min; TLC R_f 0.59 (5% EtOAc in hexanes); δ_H ($CDCl_3$) 0.01 (s, 9H, 3×CH_3), 1.12 (d, J=7.9 Hz, 2H, CH_2Si), 3.78 (m, 1H, PhCH), 4.68 (d, J=8.0 Hz, 2H, CH_2N), 7.39–7.50 (m, 5H, PhH); ν_{max} (film)/cm^{-1} 3040 (m, Ph), 2954 (s, C–H), 2884 (s, C–H), 1605 (w, Ph), 1551 (s, NO_2), 1378 (s, NO_2), 1250 (s, Si–C), 850 (s), 764 (m, Ph), 700 (s, Ph) cm^{-1}; *m/z* (EI) 237.1192 ($C_{12}H_{19}NO_2Si$ requires 237.1185), 222 ($M^{+\cdot}-15$, 2%), 190 (10), 118 (11), 117 (18), 105 (9), 104 (100), 103 (8), 91 (13), 75 (16), 73 (72).

7-*syn*-(Triethylsilyl)-2-*endo*-nitrobicyclo[2.2.1]hept-5-ene (9). A solution of freshly cracked cyclopentadiene (838 mg, 12.7 mmol, 1.0 equiv.) in THF (3.0 mL) was added dropwise at room temperature to a stirred suspension of sodium sand[14] (340 mg, 13.9 mmol, 1.1 equiv.) and THF (8.0 mL).

The reaction was stirred for 4.0 h, the resultant red mixture was cooled to 0°C. To this mixture was added dropwise a solution of triethylsilyl chloride (2.09 g, 13.9 mmol 1.1 equiv.) in THF (4.0 mL). After the reaction mixture was stirred at 0–5°C for 5.0 h, it was cautiously treated with ice–water (15 mL) and extracted with ether (10 mL×3). The combined organic layers were washed with water (10 mL×2), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure to give a pale yellow oil.

A solution of nitroethylene (1.48 g, 20.3 mmol, 1.6 equiv.) in ether (15 mL) was added dropwise to an ice-cooled and stirred ether solution of 5-(triethylsilyl)cyclopentadiene that was prepared as described above. The reaction mixture was stirred overnight, the solvents were evaporated, and the residue was purified by use of a Chromatotron (2 mm plate, 1% EtOAc in hexanes as eluant) to give pure **9** (739 mg, 2.92 mmol) as a light yellow oil in 23% yield (based on cyclopentadiene used): GC t_R 16.42 min; TLC R_f 0.55 (10% EtOAc in hexanes); δ_H ($CDCl_3$) 0.45 (q, J=7.8 Hz, 6H, 3×$SiCH_2$), 0.81 (t, J=7.8 Hz, 9H, 3×CH_3), 1.10 (s, 1H, SiCH), 1.83 (m, 1H), 2.13 (m, 1H), 3.04 (m, 1H), 3.59 (m, 1H), 5.00 (m, 1H, CHN), 5.81 (dd, J=5.7, 3.0 Hz, 1H, =CH), 6.30 (dd, J=5.7, 2.8 Hz, 1H, =CH); ν_{max} (film)/cm^{-1} 3093 (w, =C–H), 2953 (s, C–H), 2917 (s, C–H), 2875 (s, C–H), 1544 (s, NO_2), 1457 (m), 1376 (s, NO_2), 1241 (m, Si–C), 1016 (m), 718 (s) cm^{-1}; *m/z* (EI) 253.1489 ($C_{13}H_{23}NO_2Si$ requires 253.1498), 224 ($M^{\cdot+}-29$, 2%), 196 (31), 194 (39), 166 (16), 165 (28), 132 (100), 104 (43), 103 (68), 91 (13), 87 (13).

***trans*-2-[(Triethylsilyl)methyl]-1-nitrocyclopropane (15).** A solution of trimethylsulfoxonium iodide (281 mg, 1.28 mmol, 1.1 equiv.) in DMSO (5.0 mL) was added dropwise to a stirred suspension of sodium hydride (30.7 mg, 1.28 mmol, 1.1 equiv.) in DMSO (1.0 mL). After the mixture was stirred at room temperature for 4.0 h, it became clear. The solution was then cooled to 10°C and a solution of *trans*-1-nitro-3-(triethylsilyl)-1-propene (233 mg, 1.16 mmol, 1.0 equiv.) in DMSO (0.50 mL) was added dropwise. The mixture was stirred at 50°C in an oil bath for 4.0 h and then at room temperature for 12 h. Ice–water (10 mL) and ether (100 mL) were added into the reaction mixture. The ether layer was washed with water (15 mL×3), saturated aqueous NaCl (15 mL), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure. The residue was purified by use of a Chromatotron (2 mm plate, 2% EtOAc in hexanes as eluant) to give pure **15** (192 mg, 0.893 mmol) as a light green oil in 77% yield: GC t_R 13.76 min; TLC R_f 0.53 (10% EtOAc in hexanes); δ_H ($CDCl_3$) 0.42 (m, 1H), 0.56 (q, J=7.8 Hz, 6H, 3×$SiCH_2$), 0.86 (m, 1H), 0.92 (t, J=7.8 Hz, 9H, 3×CH_3), 1.01 (m, 1H), 1.88 (m, 2H), 3.97 (m, 1H, CHN); ν_{max} (film)/cm^{-1} 2955 (s, C–H), 2914 (s, C–H), 2876 (s, C–H), 1543 (s, NO_2), 1460 (m), 1366 (m, NO_2), 1238 (m, Si–C), 1073 (s), 1010 (s), 737 (s) cm^{-1}; *m/z* (EI) 215.1348 ($C_{10}H_{21}NO_2Si$ requires 215.1341), 186 ($M^{\cdot+}-29$, 2%), 132 (48), 115 (66), 104 (24), 103 (35), 87 (100), 75 (77), 63 (22), 59 (51), 54 (18).

Standard procedure for reaction of nitro compounds with a Lewis acid

To a stirred suspension of a Lewis acid (2.02 mmol, 2.0 equiv.) in dichloromethane (1.0 mL) was added dropwise a solution of nitro compound (1.01 mmol, 1.0 equiv.) in dichloromethane (0.55 mL) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 72 h, unless otherwise indicated. Ice–water (10 mL) and ether (30 mL) were then added into the reaction flask. The organic layer was washed with saturated aqueous $NaHCO_3$ (15 mL×2) and the aqueous layer was back extracted with Et_2O (15 mL×3). The combined etheral solutions were washed with saturated aqueous NaCl (25 mL), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure. The residue was purified by use of a Chromatotron.

***cis*-6-Cyclopentena[*e*]tetrahydro-1,2-oxazin-3-one (7) from 2-*endo*-Nitrobicyclo[2.2.1]-hept-5-ene (6).** The standard procedure was followed by use of titanium(IV) chloride (383 mg, 2.02 mmol, 2.0 equiv.) and **6** (140 mg, 1.01 mmol, 1.0 equiv.). After the reaction mixture was stirred at 0°C for 10 min, it was worked up and the residue was purified by use of a Chromatotron (1 mm plate, 7% EtOAc in hexanes as eluant) to give pure **7** (59.0 mg, 0.424 mmol) as a pale yellow oil in 42% yield: GC t_R 9.31 min; TLC R_f 0.29 (30% EtOAc in hexanes); δ_H ($CDCl_3$) 2.29 (m, 2H, =CCH_2), 2.78 (m, 2H, $COCH_2$), 3.13 (m, 1H, CH), 5.50 (m, 1H, CHO), 5.86 (m, 1H, =CH), 6.06 (m, 1H, =CH); ν_{max} (film)/cm^{-1} 3479 (m, N–H), 3041 (w, =C–H), 2962 (s, C–H), 2936 (s, C–H), 2855 (m, C–H), 1766 (s), 1676 (m, C=O), 1362 (m), 1173 (s), 1012 (m) cm^{-1}; *m/z* (EI) 124 ($M^{\cdot+}-15$, 9%), 95 (2), 81 (2), 80 (74), 79 (100), 77 (7), 67 (5), 65 (1), 53 (3), 51 (1).

5-(2-Nitroethyl)cyclopentadiene (10) from 7-*syn*-(Trimethylsilyl)-2-*endo*-nitrobicyclo-[2.2.1]hept-5-ene (8). The standard procedure was followed by use of aluminum chloride (267 mg, 2.02 mmol, 2.0 equiv.) and **8** (213 mg, 1.01 mmol, 1.0 equiv.). After the reaction mixture was stirred at 0°C for 5.0 min, it was worked up and the residue was purified by use of a Chromatotron (1 mm plate, 2% EtOAc in hexanes as eluant) to give pure **10** (139 mg, 0.999 mmol) as a pale yellow oil in 99% yield: GC t_R 8.67 min; TLC R_f 0.42 (10% EtOAc in hexanes); δ_H ($CDCl_3$) 2.91–3.13 (m, 3H), 4.54 (t, J=7.2 Hz, 2H, CH_2N), 6.32 (m, 4H, =CH); δ_C ($CDCl_3$) 28.42, 43.20, 75.09, 129.41, 132.26; ν_{max} (film)/cm^{-1} 3060 (m, =C–H), 2963 (s, C–H), 2925 (s, C–H), 2849 (m, C–H), 1651 (m, C=C), 1556 (s, NO_2), 1435 (s), 1379 (s, NO_2), 1088 (w), 870 (m) cm^{-1}; *m/z* (EI) 139.0624 ($C_7H_9NO_2$ requires 139.0633), 139 ($M^{\cdot+}$, 16%), 93 (15), 92 (89), 91 (100), 79 (7), 78 (18), 77 (39), 65 (15), 53 (5), 51 (5).

5-(2-Nitroethyl)cyclopentadiene (10) from 7-*syn*-(triethylsilyl)-2-*endo*-nitrobicyclo-[2.2.1]hept-5-ene (9). The above procedure was followed except that **9** (256 mg, 1.01 mmol, 1.0 equiv.) was used to replace **8**. After purification, pure **10** (94.1 mg, 0.989 mmol) was obtained in 98% yield.

Hexaethyldisiloxane from 7-*syn*-(Triethylsilyl)-2-*endo*-nitrobicyclo[2.2.1]hept-5-ene (9). The standard procedure was followed by use of titanium(IV) chloride (383 mg, 2.02 mmol, 2.0 equiv.) and **9** (255 mg, 1.01 mmol, 1.0 equiv.). After the reaction mixture was stirred overnight, it was worked up and the residue was purified by use of a

Chromatotron (1 mm plate, hexanes as eluant) to give pure hexaethyldisiloxane (102 mg, 0.414 mmol) as a colorless oil in 82% yield: GC t_R 11.41 min; TLC R_f 0.99 (hexanes); δ_H ($CDCl_3$) 0.52 (q, J=8.0 Hz, 12H, $6\times CH_2$), 0.94 (t, J=8.0 Hz, 18H, $6\times CH_3$); ν_{max} (film)/cm^{-1} 2955 (s, C–H), 2902 (s, C–H), 2876 (s, C–H), 1458 (m), 1414 (m), 1238 (m, Si–C), 1074 (s, Si–O), 1004 (s), 741 (s), 665 (m) cm^{-1}; *m*/*z* (EI) 246 ($M^{\cdot+}$, 0.5%), 218 (21), 217 (100), 190 (14), 189 (71), 161 (43), 133 (16), 105 (21), 103 (13), 59 (11).

5-Phenyl-3-isoxazolidinone (13) from *trans*-1-nitro-2-phenylcyclopropane (12). The standard procedure was followed by use of tin(IV) chloride (526 mg, 2.02 mmol, 2.0 equiv.) and **12** (165 mg, 1.01 mmol, 1.0 equiv.). After the reaction mixture was stirred overnight, it was worked up and the residue was purified by use of a Chromatotron (1 mm plate, 80% EtOAc in hexanes as eluant) to give pure **13** (128 mg, 0.788 mmol) as yellow solid in 78% yield: mp 127–129°C; GC t_R 13.25 min; TLC R_f 0.08 (80% EtOAc in hexanes); δ_H ($CDCl_3$) 2.81–2.97 (m, 2H, CH_2), 5.24 (dd, J=11, 6.8 Hz, 1H, CH), 7.24–7.36 (m, 5H, PhH); ν_{max} (film)/cm^{-1} 3419 (m, N–H), 3041 (m, Ph), 2917 (m, C–H), 1713 (s, C=O), 1630 (w, Ph), 1455 (m), 1281 (m), 1062 (m), 763 (m, Ph), 700 (s, Ph) cm^{-1}; *m*/*z* (EI) 163.0626 ($C_9H_9NO_2$ requires 163.0633), 148 ($M^{\cdot+}-15$, 78%), 174 (100), 131 (25), 103 (43), 102 (23), 91 (22), 77 (38), 76 (9), 74 (12), 51 (27).

5-Phenyl-3-isoxazolidinone (13) and 3-chloro-3-phenylpropionohydroxamic acid (14) from *trans*-1-nitro-2-phenylcyclopropane (12). The standard procedure was followed by use of aluminum chloride (267 mg, 2.02 mmol, 2.0 equiv.) and **12** (165 mg, 1.01 mmol, 1.0 equiv.). After the reaction mixture was stirred for 30 min, it was worked up and the residue was purified by use of a Chromatotron (1 mm plate, 80% EtOAc in hexanes as eluant) to give pure **13** (78.8 mg, 0.485 mmol) in 48% yield and pure **14** (46.2 mg, 0.232 mmol) as a yellow solid in 23% yield. For **14**: mp 174–176°C; GC t_R 11.60 min; TLC R_f 0.39 (80% EtOAc in hexanes); δ_H ($CDCl_3$) 2.02 (br, 1H, OH) 3.15 (dd, J=15, 6.0 Hz, 1H), 3.31 (dd, J=15, 8.8 Hz, 1H), 5.27 (dd, J=8.8, 6.0 Hz, 1H, CHCl), 7.30–7.41 (m, 5H, PhH), 8.44 (br, 1H, NH); δ_C ($CDCl_3$) 46.46, 58.48, 126.95, 128.82, 128.99, 137.64, 139.58; ν_{max} (film)/cm^{-1} 3605 (m, O–H), 3315 (s, N–H), 3040 (m, Ph), 2919 (m, C–H), 1638 (s, C=O), 1601 (m), 1454 (s), 1122 (s), 765 (m, Ph), 698 (s, Ph) cm^{-1}; *m*/*z* (EI) 181.0309 (C_9H_8ClNO requires 181.0294), 181 ($M^{\cdot+}-18$, 11%), 128 (7), 127 (32), 126 (7), 125 (100), 103 (5), 90 (5), 89 (15), 63 (6), 56 (6).

4-Nitro-1-butene (16) and hexaethyldisiloxane from *trans*-2-[(triethylsilyl)methyl]-1-nitrocyclopropane (15). The standard procedure was followed by use of **15** (217 mg, 1.01 mmol, 1.0 equiv.) and four different Lewis acids, respectively. By use of aluminum chloride (267 mg, 2.02 mmol, 2.0 equiv.), **16** (73.5 mg, 0.727 mmol) was obtained in 72% yield and hexaethyldisiloxane (117 mg, 0.475 mmol) in 94% yield; by titanium(IV) chloride (383 mg, 2.02 mmol, 2.0 equiv.), **16** (67.4 mg, 0.667 mmol) was obtained in 66% yield and hexaethyldisiloxane (98.1 mg, 0.399 mmol) in 79% yield; by boron trifluoride diethyl etherate (287 mg, 2.02 mmol, 2.0 equiv.), **16** (59.2 mg, 0.586 mmol) was obtained in 58% yield and hexaethyldisiloxane (95.7 mg, 0.389 mmol) in 77% yield; and by tin(IV) chloride (526 mg, 2.02 mmol, 2.0 equiv.), **16** (68.4 mg, 0.677 mmol) was obtained in 67% yield and hexaethyldisiloxane (107 mg, 0.434 mmol) in 86% yield. The spectroscopic and physical data of **16** are consistent with those reported.[18,19]

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