Ultrasonic Nitration of Allylsilanes by Use of Sodium Nitrite and Ceric Ammonium Nitrate

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An efficient method was developed for synthesis of a new class of compounds, 1-nitro-3-organosilyl-1-propenes. Sonication of a chloroform solution containing allylsilanes with various organosilyl groups, $NaNO_2$ (10 equiv), $Ce(NH_4)_2(NO_3)_6$ (2.0 equiv), and acetic acid (12 equiv) in a sealed tube at 600 W and 25−55 °C afforded 1-nitro-3-organosilyl-1-propenes in 51−86% yields. By the same method at 25−73 °C, various olefins, styrene, benzofuran, and indene were converted to the corresponding α,β-unsaturated nitro olefins in 54−99% yields. Advantages associated with this new nitration method include mild conditions, high regioselectivity, good to excellent yields, and a short period of reaction time.

Introduction

Placement of a silyl group at a β position of ketones can increase the quantum yield and the reaction rate of the Norrish Type I cleavage.[1] This silicon-promoted reaction could be applied in the development of novel photodegradable polymers, which are of value to electronic industry and environmental protection. Poly(olefin co-carbon monoxide),[2] polyvinylketones,[3] and carbonyl group-containing polymers are among the well recognized photodegradable polymers, and their studies have attracted much attention from polymer scientists. In our project of synthesizing silicon-containing polyketones with photodegradability (Scheme 1),[4] we needed certain 1-nitro-3-organosilyl-1-propene monomers (**1**).

Many methods can be used to convert olefins or nitroalkanes to nitro olefins.[5−7] Nevertheless, we found that none of those was applicable to synthesis of 1-nitro-3-(triisopropylsilyl)-1-propene with success, except the procedure developed by Jolibois et al.[8] Scheme 2 shows our results, in which allyltriisopropylsilane was allowed to react with nitrosyl chloride in chloroform at −60 °C. We then oxidized the resultant nitroso dimer intermediate with *m*-chloroperbenzoic acid (*m*-CPBA) to give the corresponding nitro compound. Dehydrochlorination of the β-chloro nitro compound in the presence of triethylamine or silica gel produced the target 1-nitro-3-(triisopropylsilyl)-1-propene. The overall yields, however, ranged from 17−28% only. The low yields may be due to the inefficiency of individual transformations or instability of the product toward the reaction conditions. Consequently, we investigated a new and widely applicable method that can lead olefins, especially allylsilanes, to the corresponding α,β-unsaturated nitro olefins efficiently under mild conditions.[9]

Results

Nitration of Allylsilanes and Control Experiments. To search for a new nitration method, we first treated a solution of allyltriisopropylsilane (**2**: X = $(i\text{-Pr})_3SiCH_2$) with various equivalents of sodium nitrite and an acid, including acetic acid, *p*-toluenesulfonic acid, sulfuric acid, and hydrochloric acid (see Table 1, columns 2 and 3). Reaction between sodium nitrite and an acid allows generation of the nitrating species $NO_2^{\bullet}$ through nitrous acid.[10] To avoid its expulsion, we applied the "sealed-tube technique".

We found that the presence of an oxidizing agent in situ can significantly improve the yields of the desired 1-nitro-3-(triisopropylsilyl)-1-propene (**3h**, see Table 2). Among various oxidizing agents studied, such as ceric ammonium nitrate (CAN), manganese dioxide, *m*-CPBA, and molecular oxygen, CAN gave the most appeal-

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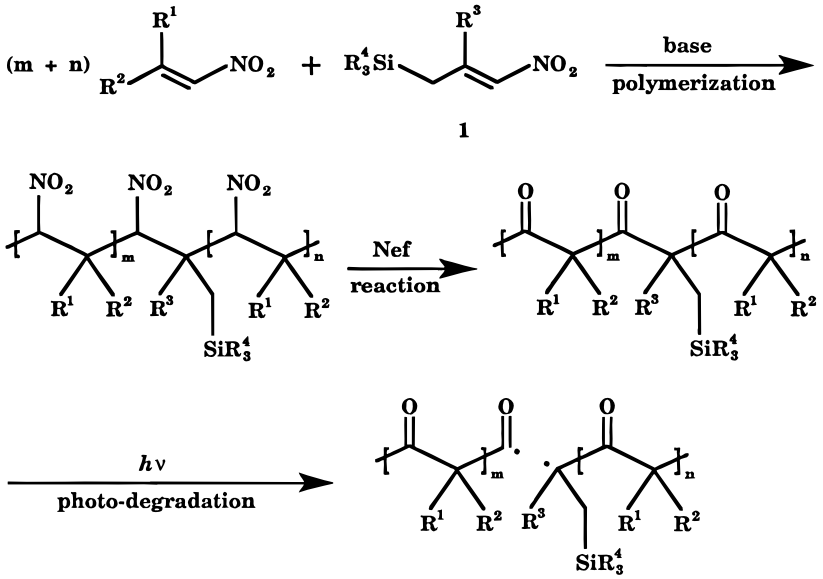
Scheme 1



Scheme 2

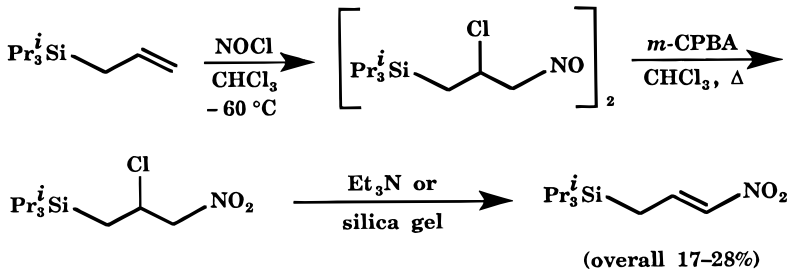


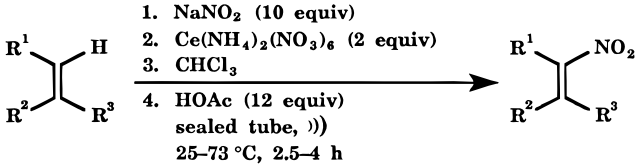
Table 1. Nitration of Allyltriisopropylsilane (2h) to *trans*-1-Nitro-3-(triisopropylsilyl)-1-propene (3h) in a Sealed Tube at 25−55 °C for 2.5 h under Various Conditions

entry	$NaNO_2$ (equiv)	acid	equiv	oxidant	equiv	solvent	ultra-sound (W)	yield (%)
1	10	HOAc	12	none	−	$CHCl_3$	600	45
2	10	TsOH	12	none	−	$CHCl_3$	600	0
3	10	H_2SO_4	12	none	−	$CHCl_3$	600	0
4	10	HCl	12	none	−	$CHCl_3$	600	0
5	10	HOAc	12	MnO_2	2	$CHCl_3$	600	25
6	10	HOAc	12	*m*-CPBA	2	$CHCl_3$	600	trace
7	10	HOAc	12	O_2	sat.	$CHCl_3$	600	14
8	5	HOAc	6	CAN	2	H_2O	600	22
9	5	HOAc	6	CAN	2	MeOH	600	trace
10	5	HOAc	6	CAN	2	CH_3CN	600	35
11	5	HOAc	6	CAN	2	EtOAc	600	18
12	5	HOAc	6	CAN	2	$CHCl_3$	none	33
13	5	HOAc	3	CAN	2	$CHCl_3$	600	trace
14	5	HOAc	6	CAN	2	$CHCl_3$	600	47
15[a]	5	HOAc	6	CAN	2	$CHCl_3$	600	14
16	5	HOAc	6	CAN	2	$CHCl_3$	300	36
17	5	HOAc	12	CAN	2	$CHCl_3$	600	46
18	10	HOAc	12	CAN	2	$CHCl_3$	600	81
19	10	HOAc	12	CAN	1	$CHCl_3$	600	63

[a] The reaction was performed in a semiclosed system under nitrogen gas.

ing results (see Table 1). Furthermore, we found that a higher yield of the desired nitro olefin was obtained by using chloroform as the solvent than by others, including water, methanol, acetonitrile, and ethyl acetate. The solubility of CAN, however, is low in chloroform. Consequently we applied ultrasound[11] up to 600 W to the heterogeneous solution of chloroform for acceleration of the reaction.

Scheme 3



By following the optimum nitration conditions (Scheme 3 and entry 18 in Table 1), we treated silicon-containing propenes **2a**−**i** sequentially with sodium nitrite (10 equiv), CAN (2.0 equiv), and acetic acid (12 equiv) in chloroform in a sealed tube. After sonication at 600 W and 25−55 °C for 2.5 h, a single α,β-unsaturated nitro olefin was obtained in each reaction (Table 2). The yields ranged from 51−86%. Those α,β-unsaturated nitro olefins showed a coupling constant of 12.8−13.8 Hz, which indicates the vicinal vinylic protons with a trans relationship.[12a] Two proton signals were observed ranging from δ 6.89−6.96 ppm and from δ 7.39−7.48 ppm, which indicate existence of a $RCH{=}CHNO_2$ moiety.[6c,13] Further evidence on nitration at the terminal sp^2 carbon was obtained from their ^{13}C NMR spectra. The products exhibited two ^{13}C signals at δ 136.9−137.4 and 143.1−144.0 ppm.[14] Results from

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(13) Cf. Seebach, D.; Knochel, P. *Helv. Chim. Acta* **1984**, *67*, 261.
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Table 2. Nitration of Olefins by Use of $NaNO_2$ (10 equiv), CAN (2.0 equiv), and HOAc (12 equiv) in Chloroform under Sonication at 600 W in a Sealed Tube To Give the Corresponding α,β-Unsaturated Nitro Olefins

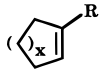
entry	alkene	X =	temp, °C	time, h	product	% yield
1	**2a**	Et_3SiCH_2	25−55	2.5	**3a**	57
2	**2b**	*i*-$PrMe_2SiCH_2$	25−55	2.5	**3b**	51
3	**2c**	(cyclohexyl)Me_2SiCH_2	25−55	2.5	**3c**	65
4	**2d**	$(Me_2HCMe_2C)Me_2SiCH_2$	25−55	2.5	**3d**	70
5	**2e**	$(n\text{-}Bu)_3SiCH_2$	25−55	2.5	**3e**	72
6	**2f**	$(n\text{-}C_6H_{13})_3SiCH_2$	25−55	2.5	**3f**	82
7	**2g**	$(Me_2CHCH_2)_3SiCH_2$	25−55	2.5	**3g**	86
8	**2h**	$(i\text{-}Pr)_3SiCH_2$	25−55	2.5	**3h**	81
9	**2i**	$(EtO)_3SiCH_2$	25−55	2.5	**3i**	53
10	**2j**	$n\text{-}C_6H_{13}$	25−73	4	**3j**	99
11	**2k**	Ph	25−73	4	**3k**	82
12	**4a**	1	25−73	4	**5a**	86
13	**4b**	2	25−73	4	**5b**	99
14	**4c**	4	25−73	4	**5c**	71
15	**6a**	O	25−73	4	**7a**	62
16[a]	**6b**	CH_2	25	0.5	**7b**	54

[a] Sonication and CAN are not required.

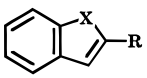
distortionless enhancement by polarization transfer experiments indicate that one proton was attached to each of the two sp^2 carbons.[12b] These NMR data along with IR and mass spectroscopic evidence allow us to identify the products as **3a**−**i** without ambiguity. Furthermore, we found that the siloxyl group in **3i** survived under the newly developed nitration conditions.

Synthesis of Non-silylated α,β-Unsaturated Nitro Olefins. Nitro olefins without a silyl group at the allylic position are normally stable under neutral conditions.[5−7] We thus applied the new nitration method shown in Scheme 3 to the preparation of non-silylated nitro olefins under the same conditions, except that the reaction temperature was higher (up to 73 °C versus 55 °C) and the reaction time was longer (4 h versus 2.5 h). Consequently, nitro olefin **3j** and β-nitrostyrene (**3k**) were obtained in 99% and 82% yields, respectively (entries 10 and 11 in Table 2). Furthermore, we were able to convert cycloalkenes **4a**−**c** to nitro olefins **5a**−**c** in good to excellent yields (71−99%, entries 12−14 in Table 2). Nevertheless, no 2-nitronorbornene was detected in the nitration of 2-norbornene.

2. R = H
3. R = NO_2



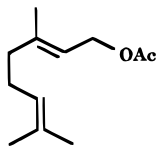
4. R = H
5. R = NO_2



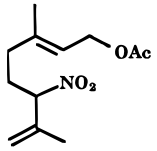
6. R = H
7. R = NO_2

Nitration also took place smoothly under the same conditions for olefins having a benzo-fused ring, as exemplified in the conversion of benzofuran (**6a**) to 2-nitrobenzofuran (**7a**) in 62% yield (entry 15 in Table 2). In addition, we found that transformation of indene (**6b**) to 2-nitroindene (**7b**) proceeded rapidly by using sodium nitrite and acetic acid in the absence of CAN and sonication (entry 16). Each of the two reactions produced regioselectively one nitro product (i.e., **7a** and **7b** individually).

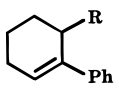
Formation of β,γ-Unsaturated Nitroalkenes. Ultrasonic nitration of geranyl acetate (**8**) with sodium nitrite, acetic acid, and CAN in chloroform at 25−73 °C in a sealed tube produced a complex mixture. Allylic nitro olefin **9**, instead of α,β-unsaturated nitro olefins, was isolated as the major product in 52% yield from the mixture. Results from this experiment provide us a clue to understand the reaction mechanism. Furthermore, the same conditions also led 1-phenyl-1-cyclohexene (**10**) to an allylic nitrocyclohexene (i.e., **11**) in 84% yield.



8



9



10. R = H
11. R = NO_2

Discussion

Formation of α,β- versus β,γ-Unsaturated Nitro Olefins: Addition versus Hydrogen Abstraction Mechanisms. Our mechanistic interpretation on synthesis of α,β-unsaturated nitro olefins is depicted in Scheme 4. Acidification of sodium nitrite can generate nitrous acid.[10] Ashmore and Tyler[15] as well as Asquith[16] reported the equilibrium between nitrous acid and a mixture of nitrogen dioxide radical ($NO_2^{\bullet}$), nitric oxide radical ($NO^{\bullet}$), and water. Furthermore, Pryor et al.[17] found that $NO_2^{\bullet}$ in high concentration can add to a carbon−carbon double bond. Accordingly, we generated the nitrating species $NO_2^{\bullet}$ from an excess of sodium nitrite and acetic acid in a sealed tube. On the other hand, we believe that the $NO^{\bullet}$ generated in situ cannot compete with $NO_2^{\bullet}$ to react with olefins on the basis of the results reported by Görsdorf et al.[18]

Addition of $NO_2^{\bullet}$ to a carbon−carbon double bond in olefins would produce the radical intermediates **12**. To minimize the reversibility of **12** to starting materials, we considered adding the one-electron oxidizing agent CAN[19] in situ. This reagent could oxidize radicals **12** to carbocationic intermediates **13**. Finally, the desired α,β-unsaturated nitro olefins **14** would be generated by elimination of an α-proton in **13**.

Alternatively, $NO_2^{\bullet}$ may abstract an allylic hydrogen atom from olefins to give allylic radicals **15** (see Scheme 4).[17] Radical coupling between allylic radicals **15** and

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(16) Asquith, P. L.; Tyler, B. J. *J. Chem. Soc. D* **1970**, 744.
(17) Pryor, W. A.; Lightsey, J. W.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 6685.
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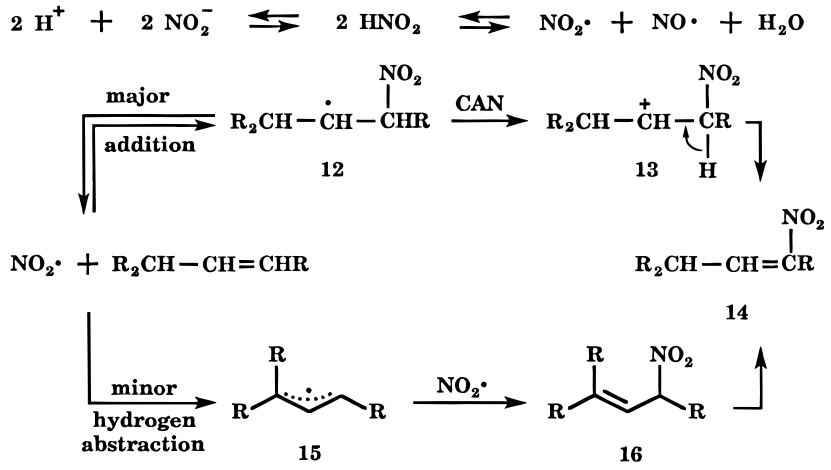
Scheme 4



$NO_2^•$ gives allylic nitro compounds **16**, which can be isomerized to thermodynamically more stable α,β-unsaturated nitro olefins **14**. In comparison with addition reaction, hydrogen abstraction is a minor pathway.[17]

The new method led various olefins to α,β-unsaturated nitro olefins **14** as the exclusive nitrated products in all reactions except two. The first reaction involves nitration of the carbon−carbon double bond attached to two methyl groups in geranyl acetate (**8**). Such a moiety provides six primary allylic hydrogen atoms for abstraction by $NO_2^•$. We thus obtained the allylic nitro olefin **9** in 52% yield. Alternatively, this olefin could be generated through intermediates **12** (see Scheme 4) by the addition process, which was followed by elimination of a γ (instead of α) methyl proton in **13**. In the second reaction, 1-phenyl-1-cyclohexene (**10**) was converted to allylic nitrocyclohexene **11**, instead of α,β-unsaturated 1-nitro-2-phenylcyclohexene. Bordwell and Garbisch[20] reported that **11** is thermodynamically more stable than 1-nitro-2-phenylcyclohexene, in which neither the nitro nor the phenyl group can conjugate effectively with the carbon−carbon double bond.

Although the two processes shown in Scheme 4 could lead olefins to nitro olefins, we cannot exclude the possibility that the nitrating step involves addition of NO_2^+ to a C−C double bond. Formation of NO_2^+ species through oxidation of $NO_2^•$ by CAN, however, is unprecedented to the best of our knowledge.

Influence of the Size of Silyl Groups on Preparation of 1-Nitro-3-organosilyl-1-propenes. The new nitration method can lead general olefins to α,β-unsaturated nitro olefins in a yield as high as 99%, as shown in entries 10 and 13 in Table 2. Application of the same conditions to synthesis of 1-nitro-3-organosilyl-1-propenes afforded **3a**−**i** in 51−86% yields. The mild nature of this newly developed method stands out in its application to the conversions of **2a**−**i** to **3a**−**i** in good yields.

We found that the yields of 1-nitro-3-organosilyl-1-propenes often depended upon the size of silyl groups (see Table 2):[21] a bulkier group gave a higher yield. Use of the new method cannot produce 1-nitro-3-organosilyl-1-propenes bearing a small silyl group, including Me_3-Si, $EtMe_2Si$, Ph_2MeSi, and $(MeO)_3Si$. Fleming and Langley[22] reported that rate of protodesilylation was faster for substrate having a smaller silyl group. Accordingly, we consider the possibility of elimination of a small silyl group located at a β position in the carbocationic intermediates **13**. Such a desilylation would interfere in generation of the desired 1-nitro-3-organosilyl-1-propenes **1**.

Regioselectivity and Advantages. Nitration of nonsymmetric compounds **2a**−**k**, **6a**, or **6b** by use of the method shown in Scheme 3 gave olefins **3a**−**k**, **7a**, and **7b**, respectively. Preferential formation of a more stable secondary, instead of a less stable primary, carboradical intermediate (e.g., **12**) is likely to be the major factor responsible for the selective formation of **3a**−**k**. In the conversions of **6a** → **7a** and **6b** → **7b**, regioselectivity may come from the generation of a benzylic radical intermediate.

Use of sodium nitrite and acetic acid to generate a nitrating agent in an organic solvent avoids handling of the highly toxic mixture of $NO_2^•$ and N_2O_4 in gas phase.[23] The newly developed sonochemical method involves simple manipulation, does not require anhydrous conditions, and is economical. Furthermore, the nitration is complete in a short period of time.

Conclusion

A new sonochemical method was developed for nitration of olefins by use of sodium nitrite, CAN, and acetic acid. The desired α,β-unsaturated nitro olefins were generated in a highly regioselective manner in good to excellent yields. This new nitration reaction is cost effective and widely applicable to various olefins, especially to allylsilanes. It also involves a short period of reaction time and mild conditions.

Experimental Section

General Procedure. Chloroform, ethyl acetate, and hexanes from Mallinckrodt Chemical Co. were dried and distilled from CaH_2. Allyl bromide from Aldrich was dried and distilled from CaH_2 and stored in septum-capped bottles under argon over molecular sieves 4A. Allyltriethoxysilane, allyltriisopro-

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pylsilane, 2,3-benzofuran, ceric ammonium nitrate (CAN), chlorocyclohexyldimethylsilane, chlorodimethylthexylsilane, chloro(isopropyl)dimethylsilane, chlorotriethylsilane, chlorotrihexylsilane, chlorotriisobutylsilane, geranyl acetate, indene, 1-phenyl-1-cyclohexene, and tributylchlorosilane were purchased from Aldrich Chemical Co. Allyltrialkylsilanes were prepared by the method of Slutsky and Kwart.[24] Cyclohexene, *cis*-cyclooctene, cyclopentene, 1-octene, sodium nitrite, and styrene were purchased from Merck Inc. Acetic acid was purchased from Alps Chemical Co. An Elma T 790 H ultrasonicator was used with ultrasonic frequency 35 KHz and generator peak output 600 W. The sealable bottles[25] from Tung Kuang Glassware Industrial Corp. were used to carry out experiments that required a closed system. 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 gravity column chromatography was carried out by use of Merck Reagents Silica Gel 60 (particle size 0.063−0.200 mm, 70−230 mesh ASTM).

Standard Procedure for Nitration of Alkenes to Conjugated Nitroalkenes. To a sealable bottle were added $NaNO_2$ (10 equiv), allyltrialkylsilane (1.0 equiv), CAN (2.0 equiv), and chloroform (7.0 mL) in sequence. Then HOAc (12 equiv) was added to the mixture in one portion, and the bottle was sealed immediately. The sealed bottle was sonicated at 600 W and 25−73 °C for 2.5−4 h. The reaction mixture was washed with saturated aqueous Na_2CO_3 (20 mL) and extracted with Et_2O (15 mL × 3). The combined ethereal solutions were washed with saturated aqueous NaCl (15 mL × 2). The mixture was then dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was chromatographed through a column (1.5 cm × 16 cm) packed with silica gel to give the desired conjugated nitroalkene.

***trans*-1-Nitro-3-(triethylsilyl)-1-propene (3a).** A mixture of $NaNO_2$ (351 mg, 5.09 mmol, 10 equiv), allyltriethylsilane (79.7 mg, 0.511 mmol, 1.0 equiv), CAN (558 mg, 1.02 mmol, 2.0 equiv), chloroform (7.8 mL), and HOAc (349 μL, 6.11 mmol, 12 equiv) was sonicated at 25−55 °C for 2.5 h. Chromatography (2% EtOAc) gave pure **3a** (58.5 mg, 0.291 mmol) as a pale yellow oil in 57% yield: GC t_R 11.18 min; TLC R_f 0.45 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.58 (q, J = 7.9 Hz, 6 H, 3 × CH_3CH_2), 0.93 (t, J = 7.9 Hz, 9 H, 3 × CH_3), 1.78 (d, J = 10.0 Hz, 2 H, CH_2C=), 6.91 (d, J = 13.2 Hz, 1 H, CHN), 7.42 (dt, J = 13.2 Hz, 10.0 Hz, 1 H, CH=CN); ^{13}C NMR ($CDCl_3$) δ 2.96, 6.78, 16.10, 136.90, 143.06; IR (neat) 3093 (w, =C−H), 2954 (s, C−H), 2911 (m, C−H), 2878 (s, C−H), 1635 (s, C=C), 1516 (s, NO_2), 1345 (s, NO_2), 1243 (w, Si−C), 1123 (m), 730 (s) cm^{-1}; MS m/z (relative intensity) 201 ($M^{\bullet+}$, 9), 173 (9), 172 (71), 156 (7), 104 (7), 103 (66), 87 (12), 76 (8), 75 (100), 63 (15). Anal. Calcd for $C_9H_{19}NO_2Si$: C, 53.73; H, 9.45; N, 6.97. Found: C, 53.82; H, 9.69; N, 7.01.

***trans*-3-(Isopropyldimethylsilyl)-1-nitro-1-propene (3b).** A mixture of $NaNO_2$ (346 mg, 5.01 mmol, 10 equiv), allylisopropyldimethylsilane (70.7 mg, 0.498 mmol, 1.0 equiv), CAN (547 mg, 0.997 mmol, 2.0 equiv), chloroform (7.0 mL), and HOAc (343 μL, 6.01 mmol, 12 equiv) was sonicated at 25−55 °C for 2.5 h. Chromatography (2% EtOAc) gave pure **3b** (47.5 mg, 0.254 mmol) as a pale yellow oil in 51% yield: GC t_R 9.14 min; TLC R_f 0.45 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 6 H, $(CH_3)_2Si$), 0.73−0.97 (m, 7 H, $CH(CH_3)_2$), 1.76 (d, J = 9.6 Hz, 2 H, CH_2), 6.91 (d, J = 13.2 Hz, 1 H, CHN), 7.40 (dt, J = 13.2 Hz, 9.6 Hz, 1 H, CH=CN); ^{13}C NMR ($CDCl_3$) δ −5.45, 13.19, 17.22, 18.40, 137.25, 143.14; IR (neat) 3108 (w, =C−H), 2949 (m, C−H), 2865 (m, C−H), 1632 (m, C=C), 1516 (s, NO_2), 1345 (s, NO_2), 1254 (m, Si−C), 1123 (m), 882 (m), 826 (m) cm^{-1}; MS m/z (relative intensity) 187 ($M^{\bullet+}$, 7), 172 (5), 145 (9), 144 (79), 77 (7), 76 (8), 75 (100), 73 (5), 61 (9), 59 (5). Anal. Calcd for $C_8H_{17}NO_2Si$: C, 51.34; H, 9.09; N, 7.49. Found: C, 51.24; H, 9.03; N, 7.60.

***trans*-3-(Cyclohexyldimethylsilyl)-1-nitro-1-propene (3c).** A mixture of $NaNO_2$ (343 mg, 4.97 mmol, 10 equiv), allylcyclohexyldimethylsilane (90.6 mg, 0.498 mmol, 1.0 equiv), CAN (545 mg, 0.994 mmol, 2.0 equiv), chloroform (6.7 mL), and HOAc (342 μL, 6.01 mmol, 12 equiv) was sonicated at 25−55 °C for 2.5 h. Chromatography (2% EtOAc) gave pure **3c** (73.5 mg, 0.324 mmol) as a pale yellow oil in 65% yield: GC t_R 14.12 min; TLC R_f 0.55 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 6 H, 2 × CH_3), 0.65−1.78 (m, 13 H), 6.89 (d, J = 13.2 Hz, 1 H, CHN), 7.42 (dt, J = 13.2 Hz, 9.8 Hz, 1 H, CH=CN); ^{13}C NMR ($CDCl_3$) δ −5.51, 18.28, 24.99, 26.63, 27.08, 27.69, 137.09, 143.25; IR (neat) 3091 (w, =C−H), 2920 (m, C−H), 2847 (m, C−H), 1632 (m, C=C), 1516 (s, NO_2), 1446 (m), 1347 (s, NO_2), 1252 (m, Si−C), 1121 (m), 834 (s) cm^{-1}; MS m/z (relative intensity) 212 ($M^{\bullet+}$ − 15, 1), 145 (11), 144 (100), 128 (4), 77 (7), 76 (6), 75 (75), 61 (10), 59 (5), 55 (4); HRMS calcd for $C_{11}H_{21}NO_2Si$ 227.1341, found 227.1354. Anal. Calcd for $C_{11}H_{21}NO_2Si$: C, 58.15; H, 9.25; N, 6.17. Found: C, 58.34; H, 9.57; N, 6.16.

***trans*-3-(Dimethylthexylsilyl)-1-nitro-1-propene (3d).** A mixture of $NaNO_2$ (347 mg, 5.03 mmol, 10 equiv), allyldimethylthexylsilane (92.6 mg, 0.503 mmol, 1.0 equiv), CAN (552 mg, 1.01 mmol, 2.0 equiv), chloroform (7.7 mL), and HOAc (345 μL, 6.04 mmol, 12 equiv) was sonicated at 25−55 °C for 2.5 h. Chromatography (2% EtOAc) gave pure **3d** (80.6 mg, 0.352 mmol) as a pale yellow oil in 70% yield: GC t_R 15.27 min; TLC R_f 0.51 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 6 H, $(CH_3)_2Si$), 0.82−0.87 (m, 12 H, 4 × CH_3), 1.59 (m, 1 H, Me_2CH), 1.79 (d, J = 9.6 Hz, 2 H, CH_2), 6.90 (d, J = 13.2 Hz, 1 H, CHN), 7.41 (dt, J = 13.2 Hz, 9.6 Hz, 1 H, CH=CN); ^{13}C NMR ($CDCl_3$) δ −4.02, 18.40, 18.77, 20.62, 23.80, 34.55, 137.18, 143.55; IR (neat) 3088 (w, =C−H), 2956 (s, C−H), 2851 (m, C−H), 1632 (m, C=C), 1517 (s, NO_2), 1468 (m), 1345 (s, NO_2), 1255 (m, Si−C), 1124 (m), 827 (m) cm^{-1}; MS m/z (relative intensity) 144 ($M^{\bullet+}$ − 85, 31), 99 (13), 85 (5), 84 (6), 76 (4), 75 (53), 73 (100), 69 (5), 61 (5), 59 (13). Anal. Calcd for $C_{11}H_{23}NO_2Si$: C, 57.64; H, 10.04; N, 6.11. Found: C, 57.49; H, 10.00; N, 6.43.

***trans*-1-Nitro-3-(tributylsilyl)-1-propene (3e).** A mixture of $NaNO_2$ (341 mg, 4.94 mmol, 10 equiv), allyltributylsilane (118 mg, 0.493 mmol, 1.0 equiv), CAN (542 mg, 0.988 mmol, 2.0 equiv), chloroform (6.1 mL), and HOAc (339 μL, 5.93 mmol, 12 equiv) was sonicated at 25−55 °C for 2.5 h. Chromatography (2% EtOAc) gave pure **3e** (101 mg, 0.355 mmol) as a pale yellow oil in 72% yield: GC t_R 18.86 min; TLC R_f 0.58 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.56 (t, J = 8.0 Hz, 6 H, 3 × $PrCH_2Si$), 0.86 (t, J = 7.2 Hz, 9 H, 3 × CH_3), 1.28 (m, 12 H), 1.76 (d, J = 9.6 Hz, 2 H, CH_2C=), 6.89 (d, J = 13.2 Hz, 1 H, CHN), 7.39 (dt, J = 13.2 Hz, 9.6 Hz, 1 H, CH=CN); ^{13}C NMR ($CDCl_3$) δ 11.79, 13.52, 17.37, 25.69, 26.45, 136.97, 143.34; IR (neat) 3081 (w, =C−H), 2956 (s, C−H), 2912 (s, C−H), 2880 (s, C−H), 1633 (m, C=C), 1519 (s, NO_2), 1461 (m), 1346 (s, NO_2), 1257 (w, Si−C), 1123 (m), 883 (m) cm^{-1}; MS m/z (relative intensity) 228 ($M^{\bullet+}$ − 57, 86), 159 (10), 143 (46), 103 (100), 101 (31), 87 (36), 85 (21), 73 (17), 61 (41), 59 (60); HRMS calcd for $C_{15}H_{30}NO_2Si$ ($M^{\bullet+}$ − H) 284.2046, found 284.2046. Anal. Calcd for $C_{15}H_{31}NO_2Si$: C, 63.16; H, 10.88; N, 4.91. Found: C, 62.75; H, 11.06; N, 5.17.

***trans*-1-Nitro-3-(trihexylsilyl)-1-propene (3f).** A mixture of $NaNO_2$ (332 mg, 4.81 mmol, 10 equiv), allyltrihexylsi-

(24) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.
(25) Loewenthal, H. J. E.; Zass, E. *A Guide for the Perplexed Organic Experimentalist*, 2nd ed.; Wiley: New York, 1990; p 118.

lane (156 mg, 0.482 mmol, 1.0 equiv), CAN (528 mg, 0.962 mmol, 2.0 equiv), chloroform (5.8 mL), and HOAc (331 μL, 5.77 mmol, 12 equiv) was sonicated at 25−55 °C for 2.5 h. Chromatography (2% EtOAc) gave pure **3f** (155 mg, 0.419 mmol) as a pale yellow oil in 87% yield: GC t_R 23.70 min; TLC R_f 0.71 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.55 (t, J = 5.2 Hz, 6 H, 3 × CH_2CH_2Si), 0.86 (t, J = 6.6 Hz, 9 H, 3 × CH_3), 1.22−1.27 (m, 24 H), 1.76 (d, J = 9.6 Hz, 2 H, CH_2C=), 6.89 (d, J = 13.8 Hz, 1 H, CHN), 7.39 (dt, J = 13.8 Hz, 9.6 Hz, 1 H, CH=CN); ^{13}C NMR ($CDCl_3$) δ 12.22, 13.98, 17.47, 22.50, 23.50, 31.36, 33.28, 137.06, 143.34; IR (neat) 3096 (w, =C−H), 2950 (s, C−H), 2909 (s, C−H), 2881 (s, C−H), 1722 (m), 1633 (m, C=C), 1520 (s, NO_2), 1462 (m), 1346 (s, NO_2), 1257 (m, Si−C) cm^{-1}; MS m/z (relative intensity) 284 ($M^{\bullet+}$ − 85, 100), 199 (32), 131 (31), 115 (26), 113 (28), 99 (8), 85 (22), 83 (10), 73 (16), 59 (18); HRMS calcd for $C_{21}H_{43}NO_2Si$ 369.3063, found 369.3058. Anal. Calcd for $C_{21}H_{43}NO_2Si$: C, 68.29; H, 11.65; N, 3.79. Found: C, 68.66; H, 11.94; N, 3.86.

***trans*-1-Nitro-3-(triisobutylsilyl)-1-propene (3g).** A mixture of $NaNO_2$ (344 mg, 4.98 mmol, 10 equiv), allyltriisobutylsilane (118 mg, 0.496 mmol, 1.0 equiv), CAN (546 mg, 0.996 mmol, 2.0 equiv), chloroform (6.7 mL), and HOAc (342 μL, 5.98 mmol, 12 equiv) was sonicated at 25−55 °C for 2.5 h. Chromatography (2% EtOAc) gave pure **3g** (122 mg, 0.428 mmol) as a pale yellow oil in 86% yield: GC t_R 17.78 min; TLC R_f 0.70 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.61 (d, J = 7.2 Hz, 6 H, 3 × i-$PrCH_2$), 0.93 (d, J = 6.2 Hz, 18 H, 6 × CH_3), 1.70−1.84 (m, 5 H, 3 × Me_2CH + CH_2C=), 6.90 (d, J = 13.2 Hz, 1 H, CHN), 7.40 (dt, J = 13.2 Hz, 9.6 Hz, 1 H, CH=CN); ^{13}C NMR ($CDCl_3$) δ 19.40, 23.99, 24.68, 26.44, 137.42, 143.43; IR (neat) 3085 (w, =C−H), 2957 (s, C−H), 2923 (s, C−H), 2883 (s, C−H), 1634 (m, C=C), 1557 (m), 1518 (s, NO_2), 1463 (m), 1347 (s, NO_2), 1257 (w, Si−C) cm^{-1}; MS m/z (relative intensity) 228 ($M^{\bullet+}$ − 57, 54), 212 (27), 199 (27), 143 (68), 103 (79), 101 (38), 87 (46), 73 (27), 61 (78), 59 (100); HRMS calcd for $C_{15}H_{31}NO_2Si$ 285.2124, found 285.2148. Anal. Calcd for $C_{15}H_{31}NO_2Si$: C, 63.16; H, 10.88; N, 4.91. Found: C, 62.73; H, 11.00; N, 5.23.

***trans*-1-Nitro-3-(triisopropylsilyl)-1-propene (3h).** A mixture of $NaNO_2$ (352 mg, 5.10 mmol, 10 equiv), allyltriisopropylsilane (101 mg, 0.509 mmol, 1.0 equiv), CAN (560 mg, 1.02 mmol, 2.0 equiv), chloroform (7.5 mL), and HOAc (351 μL, 6.12 mmol, 12 equiv) was sonicated at 25−55 °C for 2.5 h. Chromatography (2% EtOAc) gave pure **3h** (99.8 mg, 0.412 mmol) as a pale yellow oil in 81% yield: GC t_R 16.44 min; TLC R_f 0.55 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.02−1.11 (m, 21 H), 1.83 (d, J = 9.6 Hz, 2 H, CH_2), 6.94 (d, J = 12.8 Hz, 1 H, CHN), 7.48 (dt, J = 12.8 Hz, 9.6 Hz, 1 H, CH=CN); ^{13}C NMR ($CDCl_3$) δ 11.10, 14.17, 18.46, 137.29, 143.98; IR (neat) 3104 (w, =C−H), 2949 (s, C−H), 2865 (s, C−H), 1632 (s, C=C), 1517 (s, NO_2), 1465 (m), 1343 (s, NO_2), 1248 (m, Si−C), 1127 (m), 882 (m) cm^{-1}; MS m/z (relative intensity) 200 ($M^{\bullet+}$ − 43, 70), 157 (27), 115 (44), 103 (41), 87 (49), 77 (22), 75 (61), 73 (56), 61 (43), 59 (100); HRMS calcd for $C_{12}H_{25}NO_2Si$ 243.1654, found 243.1658. Anal. Calcd for $C_{12}H_{25}NO_2Si$: C, 59.26; H, 10.29; N, 5.76. Found: C, 59.12; H, 10.36; N, 5.82.

***trans*-1-Nitro-3-(triethoxysilyl)-1-propene (3i).** A mixture of $NaNO_2$ (339 mg, 4.91 mmol, 10 equiv), allyltriethoxysilane (101 mg, 0.491 mmol, 1.0 equiv), CAN (539 mg, 0.982 mmol, 2.0 equiv), chloroform (6.8 mL), and HOAc (337 μL, 5.89 mmol, 12 equiv) was sonicated at 25−55 °C for 2.5 h. Chromatography (5% Et_2O) gave pure **3i** (64.9 mg, 0.261 mmol) as a pale yellow oil in 53% yield: TLC R_f 0.35 (20% ether); ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7.0 Hz, 9 H, 3 × CH_3), 1.80 (d, J = 8.8 Hz, 2 H, CH_2C=), 3.82 (q, J = 7.0 Hz, 6 H, 3 × CH_2O), 6.96 (d, J = 13.2 Hz, 1 H, CHN), 7.42 (dt, J = 13.2 Hz, 8.8 Hz, 1 H, CH=CN); ^{13}C NMR ($CDCl_3$) δ 18.13, 58.52, 89.33, 137.42, 144.01; IR (neat) 3099 (w, =C−H), 2975 (m, C−H), 2924 (m, C−H), 1638 (m, C=C), 1520 (s, NO_2), 1348 (s, NO_2), 1251 (w, Si−C), 1093 (s, Si−O), 960 (m), 734 (m) cm^{-1}; MS m/z (relative intensity) 249 ($M^{\bullet+}$, 3), 164 (27), 163 (100), 135 (52), 119 (78), 107 (40), 91 (23), 79 (58), 63 (19), 45 (13). Anal. Calcd for $C_9H_{19}NO_5Si$: C, 43.37; H, 7.63; N, 5.62. Found: C, 43.21; H, 7.98; N, 5.77.

***trans*-1-Nitro-1-octene (3j).** A mixture of $NaNO_2$ (357 mg, 5.17 mmol, 10 equiv), 1-octene (57.8 mg, 0.515 mmol, 1.0 equiv), CAN (567 mg, 1.03 mmol, 2.0 equiv), chloroform (7.6 mL), and HOAc (355 μL, 6.21 mmol, 12 equiv) was sonicated at 25−73 °C for 4 h. Chromatography (2% EtOAc) gave pure **3j** (80.1 mg, 0.510 mmol) as a pale yellow oil in 99% yield: GC t_R 10.95 min; TLC R_f 0.55 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3 H, CH_3), 1.27−1.55 (m, 8 H), 2.25 (m, 2 H), 6.96 (d, J = 14 Hz, 1 H, CHN), 7.26 (m, 1 H, CH=CN); IR (neat) 3104 (w, =C−H), 2935 (s, C−H), 2860 (s, C−H), 1649 (w, C=C), 1526 (s, NO_2), 1462 (m), 1352 (s, NO_2), 958 (m), 836 (m), 729 (m) cm^{-1}; MS m/z (relative intensity) 157 ($M^{\bullet+}$, 0.2), 109 (27), 83 (23), 81 (60), 71 (20), 70 (22), 69 (42), 68 (19), 67 (100), 57 (21), 55 (77). Its spectroscopic characteristics are consistent with those of the same compound reported.[26]

***trans*-β-Nitrostyrene (3k).** A mixture of $NaNO_2$ (353 mg, 5.12 mmol, 10 equiv), styrene (53.3 mg, 0.512 mmol, 1.0 equiv), CAN (562 mg, 1.02 mmol, 2.0 equiv), chloroform (7.2 mL), and HOAc (351 μL, 6.14 mmol, 12 equiv) was sonicated at 25−73 °C for 4 h. Chromatography (2% EtOAc) gave pure **3k** (62.7 mg, 0.421 mmol) as a yellow crystal in 82% yield: mp 57−58 °C (lit.[27] mp 56−58 °C); GC t_R 12.04 min; TLC R_f 0.40 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 7.42−7.59 (m, 6 H, PhH + CHN), 7.98 (d, J = 14 Hz, 1 H, CH=CN); IR (neat) 3109 (m, =C−H), 1631 (m, C=C), 1577 (m, Ph), 1509 (s, NO_2), 1448 (s, Ph), 1344 (s, NO_2), 1263 (m), 967 (m), 770 (m, Ph), 736 (m, Ph) cm^{-1}; MS m/z (relative intensity) 149 ($M^{\bullet+}$, 74), 132 (17), 103 (31), 102 (75), 91 (58), 77 (100), 76 (16), 66 (20), 65 (19), 51 (34). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.[28]

1-Nitro-1-cyclopentene (5a). A mixture of $NaNO_2$ (329 mg, 4.77 mmol, 10 equiv), cyclopentene (32.6 mg, 0.478 mmol, 1.0 equiv), CAN (523 mg, 0.954 mmol, 2.0 equiv), chloroform (6.6 mL), and HOAc (327 μL, 5.72 mmol, 12 equiv) was sonicated at 25−73 °C for 4 h. Chromatography (2% EtOAc) gave pure **5a** (46.5 mg, 0.411 mmol) as a pale yellow oil in 86% yield: GC t_R 6.69 min; TLC R_f 0.35 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.10−2.15 (m, 2 H), 2.57−2.62 (m, 2 H), 2.80−2.86 (m, 2 H), 6.98 (m, 1 H, CH); IR (neat) 3072 (w, =C−H), 2960 (m, C−H), 2867 (m, C−H), 1641 (m, C=C), 1511 (s, NO_2), 1549 (s), 1447 (m), 1359 (s, NO_2), 1335 (m), 1279 (m) cm^{-1}; MS m/z (relative intensity) 113 ($M^{\bullet+}$, 100), 83 (56), 68 (5), 67 (46), 66 (42), 65 (67), 63 (9), 62 (6), 55 (31), 51(6). Its spectroscopic characteristics are consistent with those of the same compound reported.[29]

1-Nitro-1-cyclohexene (5b). A mixture of $NaNO_2$ (321 mg, 4.65 mmol, 10 equiv), cyclohexene (38.3 mg, 0.466 mmol, 1.0 equiv), CAN (511 mg, 0.931 mmol, 2.0 equiv), chloroform (6.1 mL), and HOAc (319 μL, 5.58 mmol, 12 equiv) was sonicated at 25−73 °C for 4 h. Chromatography (2% EtOAc) gave pure **5b** (58.6 mg, 0.461 mmol) as a pale yellow oil in 99% yield: GC t_R 9.19 min; TLC R_f 0.50 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.57 (m, 2 H), 1.71 (m, 2 H), 2.27 (m, 2 H), 2.50 (m, 2 H), 7.24 (m, 1 H, CH); IR (neat) 3080 (w, =C−H), 2942 (m, C−H), 2867 (m, C−H), 1667 (m, C=C), 1515 (s, NO_2), 1442 (m), 1336 (s, NO_2), 1056 (m), 927 (m), 822 (m) cm^{-1}; MS m/z (relative intensity) 127 ($M^{\bullet+}$, 10), 97 (17), 81 (100), 80 (10), 79 (73), 77 (20), 55 (12), 53 (41), 52 (8), 51 (14). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.[28]

1-Nitro-1-cyclooctene (5c). A mixture of $NaNO_2$ (358 mg, 5.19 mmol, 10 equiv), cyclooctene (57.3 mg, 0.520 mmol, 1.0 equiv), CAN (569 mg, 1.04 mmol, 2.0 equiv), chloroform (7.4 mL), and HOAc (356 μL, 6.23 mmol, 12 equiv) was sonicated

(26) Sircar, J. C.; Meyers, A. I. *J. Org. Chem.* **1967**, *32*, 4134.
(27) *Catalog Handbook of Fine Chemicals;* Aldrich Chemical: Milwaukee, 1994−1995; p 1055.
(28) Compounds are available from Aldrich Chemical Co.
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at 25−73 °C for 4 h. Chromatography (2% EtOAc) gave pure **5c** (57.2 mg, 0.369 mmol) as a pale yellow oil in 71% yield: GC t_R 10.98 min; TLC R_f 0.45 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.38−1.76 (m, 8 H), 2.31 (m, 2 H), 2.73 (t, J = 6.3 Hz, 2 H), 7.28 (t, J = 8.8 Hz, 1 H, CH); IR (neat) 3072 (w, =C−H), 2931 (s, C−H), 2859 (m, C−H), 1669 (w, C=C), 1548 (s, NO_2), 1518 (s), 1454 (m), 1345 (s, NO_2), 822 (m), 746 (m) cm^{-1}; MS m/z (relative intensity) 155 ($M^{\bullet+}$, 0.1), 109 (40), 81 (15), 79 (16), 77 (8), 68 (6), 67 (100), 65 (8), 55 (20), 53 (7). Its spectroscopic characteristics are consistent with those of the same compound reported.[30]

2-Nitrobenzofuran (7a). A mixture of $NaNO_2$ (362 mg, 5.25 mmol, 10 equiv), benzofuran (62.3 mg, 0.527 mmol, 1.0 equiv), CAN (576 mg, 1.05 mmol, 2.0 equiv), chloroform (7.7 mL), and HOAc (359 μL, 6.29 mmol, 12 equiv) was sonicated at 25−73 °C for 4 h. Chromatography (5% EtOAc) gave pure **7a** (53.3 mg, 0.327 mmol) as a yellow solid in 62% yield: mp 135−136 °C (lit.[31] mp 135 °C); GC t_R 12.36 min; TLC R_f 0.45 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 7.41 (m, 1 H), 7.56−7.62 (m, 2 H), 7.66 (s, 1 H), 7.75 (d, J = 8.0 Hz, 1 H); IR (neat) 3144 (w, =C−H), 1603 (m, C=C), 1561 (s, NO_2), 1516 (m, Ph), 1478 (m, Ph), 1442 (m), 1371 (s, NO_2), 1244 (s, C−O), 832 (m, Ph), 752 (m, Ph) cm^{-1}; MS m/z (relative intensity) 164 ($M^{\bullet+}$ + 1, 9), 163 (100), 133 (62), 105 (27), 89 (56), 77 (31), 63 (46), 62 (20), 61 (7), 51 (19). Its spectroscopic characteristics are consistent with those of the same compound reported.[31]

2-Nitroindene (7b). A chloroform solution (6.9 mL) containing $NaNO_2$ (347 mg, 5.02 mmol, 10 equiv), indene (58.2 mg, 0.501 mmol, 1.0 equiv), and HOAc (344 μL, 6.02 mmol, 12 equiv) was stirred at room temperature for 0.5 h. Chromatography (2% EtOAc) gave pure **7b** (43.6 mg, 0.271 mmol) as a yellow solid in 54% yield: mp 140−142 °C (lit.[32] mp 140−142 °C); GC t_R 11.77 min; TLC R_f 0.40 (20% EtOAc); ^{1}H NMR ($CDCl_3$) δ 4.01 (s, 2 H, CH_2), 7.46−7.58 (m, 4 H, PhH), 7.95 (d, J = 6.8 Hz, 1 H); IR (neat) 2960 (m, C−H), 2920 (m, C−H), 1624 (m), 1600 (m, C=C), 1490 (s, NO_2), 1403 (m), 1367 (m), 1330 (s, NO_2), 821 (m, Ph), 787 (m, Ph) cm^{-1}; MS m/z (relative intensity) 161 ($M^{\bullet+}$, 1), 158 (100), 157 (37), 130 (35), 129 (45), 116 (79), 103 (81), 102 (27), 89 (20), 76 (24). Its spectroscopic characteristics are consistent with those of the same compound reported.[33]

***trans*-3,7-Dimethyl-6-nitro-2,7-octadien-1-yl Acetate (9).** A mixture of $NaNO_2$ (365 mg, 5.29 mmol, 10 equiv), geranyl acetate (103 mg, 0.528 mmol, 1.0 equiv), CAN (581 mg, 1.06 mmol, 2.0 equiv), chloroform (8.1 mL), and HOAc (363 μL, 6.35 mmol, 12 equiv) was sonicated at 25−73 °C for 4 h. Chromatography (2% EtOAc) gave pure **9** (66.3 mg, 0.275 mmol) as a pale yellow oil in 52% yield: GC t_R 15.89 min; TLC R_f 0.41 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.69 (s, 3 H, CH_3), 1.78 (s, 3 H, CH_3), 1.87−2.13 (m, 3 H), 2.03 (s, 3 H, $COCH_3$), 2.24−2.35 (m, 1 H), 4.56 (d, J = 7.1 Hz, 2 H, OCH_2), 4.86 (t, J = 7.4 Hz, 2 H, CHN), 5.14 (s, 1 H), 5.15 (s, 1 H), 5.34 (t, J = 7.1 Hz, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ 15.76, 17.67, 20.40, 28.45, 35.00, 60.55, 91.66, 118.21, 119.94, 138.27, 138.97, 170.38; IR (neat) 2934 (s, C−H), 1735 (s, C=O), 1670 (m, C=C), 1553 (s, NO_2), 1440 (m), 1375 (s, NO_2), 1241 (s), 1025 (s, C−O), 955 (m), 720 (m) cm^{-1}; MS m/z (relative intensity) 195 ($M^{\bullet+}$ − 46, 1) 135 (41), 119 (33), 107 (65), 93 (79), 84 (100), 68 (38), 67 (52), 55 (37), 53 (25); HRMS calcd for $C_{12}H_{19}NO_4$ 241.1314, found 241.1298. Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.75; H, 7.88; N, 5.81. Found: C, 59.72; H, 8.06; N, 6.09. Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.75; H, 7.88; N, 5.81. Found: C, 59.72; H, 8.06; N, 6.09.

6-Nitro-1-phenylcyclohexene (11).[20] A mixture of $NaNO_2$ (349 mg, 5.06 mmol, 10 equiv), 1-phenyl-1-cyclohexene (80.1 mg, 0.507 mmol, 1.0 equiv), CAN (555 mg, 1.01 mmol, 2.0 equiv), chloroform (7.4 mL), and HOAc (347 μL, 6.07 mmol, 12 equiv) was sonicated at 25−73 °C for 4 h. Chromatography (2% EtOAc) gave pure **11** (86.5 mg, 0.426 mmol) as a pale yellow oil in 84% yield: GC t_R 16.25 min; TLC R_f 0.38 (10% EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.72−2.49 (m, 6 H), 5.58 (m, 1 H, CHN), 6.44 (t, J = 4.4 Hz, 1 H, PhC=CH), 7.21−7.36 (m, 5 H, PhH); IR (neat) 3040 (m, =C−H), 2942 (m, C−H), 1598 (m, Ph), 1547 (s, NO_2), 1517 (s, Ph), 1445 (m), 1355 (s, NO_2), 1158 (m, Ph), 1076 (m, Ph), 760 (m, Ph) cm^{-1}; MS m/z (relative intensity) 204 ($M^{\bullet+}$ + 1, 4), 159 (10), 158 (73), 142 (16), 141 (16), 129 (34), 115 (31), 91 (100), 79 (17), 77 (17).

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