α-Nitro Keto Hydrazone and Keto Imine Dianions. Synthetic Equivalents for the Nitroalkene d³ Synthon

Scott E. Denmark,*[1a] Jeffrey A. Sternberg,[1b] and Rainer Lueoend

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Received October 14, 1987

A general method for the preparation of 3-substituted nitrocycloalkenes has been developed. 2-Nitrocycloalkanones are transformed into either α-nitro *N,N*-dimethylhydrazones or α-nitro cyclohexylimines, which exist exclusively in the *aci*-nitro form. Double deprotonation of these materials with *sec*-BuLi produces highly reactive dianions which can be alkylated with methyl, allyl, *n*-butyl, isopropyl, or 4-hexenyl iodides in excellent yields. The alkylation occurred uniformly next to the hydrazone or imine function. The alkylated α-nitro hydrazones are converted to nitroalkenes by reduction with $NaBH_4$ followed by elimination induced by heating (120 °C) with acetic anhydride. The alkylated α-nitro imines undergo facile reduction–elimination with $NaBH_4/CeCl_3$ at room temperature. The overall yield for 2-nitro ketone to nitroalkene transformation ranged from 35% to 44% for the hydrazone method and from 19% to 39% for the imine method.

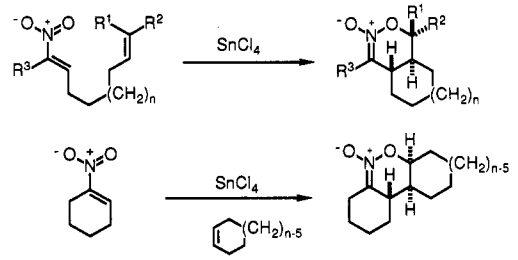
We have reported recently the use of nitroalkenes as 4π components in [4 + 2]-cycloadditions. These reactions have been shown to succeed both intramolecularly[2a] and intermolecularly[2b] (Scheme I) with unactivated olefins in the presence of $SnCl_4$. As part of an ongoing program to define the scope and limitations of these reactions, we became interested in the intramolecular version with cyclic nitroalkenes (Scheme II). We have previously described successful cycloadditions of this structural type with nitrosoalkenes[3a] and vinylnitrosonium cations (VNC's).[3b] However, the general superiority of nitroalkenes as heterodienes provided impetus for this study. One of the disadvantages of the nitrosoalkenes and VNC's is the relatively lengthy syntheses of the stable precursors of the reactive, in situ generated heterodienes. Since nitroalkenes are stable functions, we hoped to be able to prepare the cyclization substrates in a short, convergent fashion, which allowed for flexibility in the choice of ring size (*n*) and side-chain length (*m*) (Scheme III). We have found that many of the methods for synthesis of cyclic nitroalkenes[4] were not applicable and report in this paper a new, general synthesis of 3-substituted 1-nitrocycloalkenes.

Results

A. Initial Studies. At the outset we conceived of four distinct approaches to fulfill the requirements of efficiency and generality in the construction of I. These approaches fell into two classes. The first involved introduction of the nitroalkene function (or its equivalent) on an intact carbon skeleton, while the second used a masked or reactive form of the nitroalkene to couple the ring and side chain. These four approaches are summarized in Scheme IV.

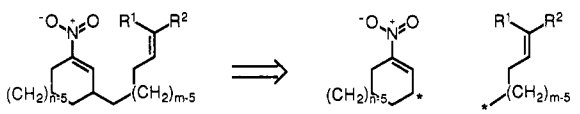
The first strategy (path A) was designed to introduce a nitro group by nitration of the alkylated cycloalkanone

Scheme I

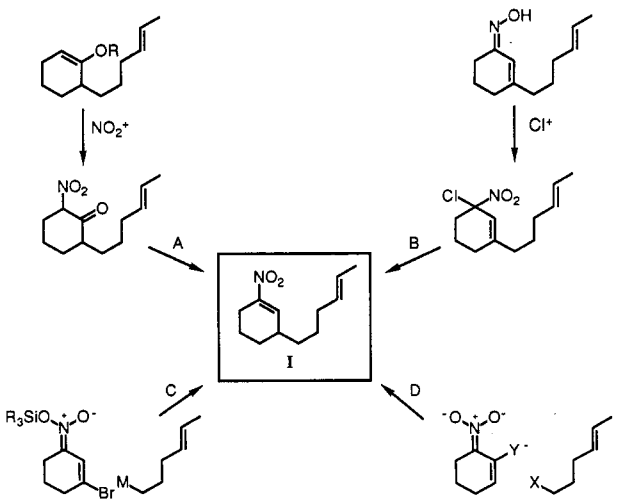


Scheme II

Scheme III



Scheme IV



(1) (a) Fellow of the A. P. Sloan Foundation (1985–1989). NSF Presidential Young Investigator (1985–1990). (b) Taken in part from: Sternberg, J. A. Ph.D. Thesis, University of Illinois, Urbana, 1987.

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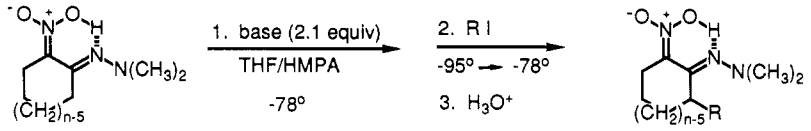
Table I. Alkylations of Dianions from 1-3



1-3 4-6

entry	n	educt	base	R	product	yield,[a] %	(crude),[b] %
1	6	1	*sec*-BuLi	CH_3	**4a**	86	(98)
2	6	1	*sec*-BuLi	CH_2=$CHCH_2$	**4b**	81	(98)
3	6	1	*sec*-BuLi	$(CH_3)_2CH$	**4c**	72	(84)
4	6	1	*sec*-BuLi	$CH_3(CH_2)_3$	**4d**	80	(98)
5	6	1	*sec*-BuLi	CH_3CH=$CH(CH_2)_3$	**4e**	84[c]	
6	5	2	*t*-BuLi	CH_3	**5a**	82	
7	7	3	*t*-BuLi	CH_3	**6a**	54[d]	

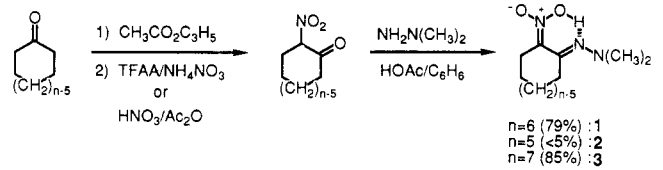
[a] Yield of analytically pure material from chromatography and/or crystallization. [b] Yield of crystalline material after aqueous workup. [c] On a 5.0-g scale, 80% yield after recrystallization. [d] After chromatography and distillation.

enolate or enol derivative.[5] Reduction and elimination of the resulting nitro ketone[4n] would provide the target nitroalkene. All attempts with various nitrating agents ($nAmONO_2$[6a] /R = K^+; $NO_2^+BF_4^-$[6b]/R = TMS or Ac, $CF_3CO_2NO_2$[6c] or $CH_3CO_2NO_2$[6d]/R = TMS or Ac) failed due to over nitration, ring cleavage, and nitration of the side chain. The second approach (path B) was based on the known oxidation of unsaturated oximes to nitroalkenes.[4h] This route also failed due to competing oxidation of the side chain with even the mildest oxidants.

A carbon-constructive approach, path C, was conceived in a conjugate substitution of a β-bromo nitronate ester. However, we found that 3-bromo-1-nitrocyclohexene[4g] underwent a facile coupling reaction upon attempted formation of the silyl nitronate. The second constructive approach (path D) involving alkylation of a nitro ketone dianion appeared highly attractive due to its simplicity, convergence, and potential generality. However, Zajac has reported this to be a poor reaction even with methyl iodide.[6b] Apparently, the poor nucleophilicity of the dianion and rapid proton transfer foil the alkylation. Since it is well known that the anions derived from hydrazones[7] and imines[7c,8] are more nucleophilic and less prone to proton transfer, we chose to investigate the chemistry of α-nitro hydrazones and α-nitro imines,[9] their derived dianions, and their transformations into nitroalkenes.

B. α-Nitro Hydrazones. 1. 2-Nitrocycloalkanone *N,N*-Dimethylhydrazones (1-3). To begin our study we selected the cyclohexanone derivative 1 to survey the feasibility of the dianion alkylation. The synthesis of 1 was short and efficient (Scheme V). Nitration of 1-cyclohexenyl acetate according to Zajac,[6c] afforded 2-nitrocyclohexanone as a 60:40 mixture of the *aci*-nitro and nitro tautomers. Optimum conditions for the hydrazonation with *N,N*-dimethylhydrazine employed 1 equiv of acetic acid in a nonnucleophilic solvent (benzene) to afford yellow, crystalline 1 in 79% yield. In the absence of acetic acid, a significant amount of hydrazide resulting from a retro nitro-Dieckman reaction was observed. The use of methanol as solvent led to an acid-catalyzed ring opening to form methyl 6-nitrohexanoate as a byproduct. Under proper conditions, 1 could be prepared in three steps from cyclohexanone in 63% yield without chromatography.

Scheme V



In contrast to the known tosylhydrazone,[10a] 1 exists exclusively in the *aci*-nitro form (OH ($CDCl_3$), 11.24 ppm). The preferred tautomeric structure of aminonitroalkenes (nitro enamines) has been the subject of extensive spectroscopic study.[9,10b] For the neutral nitro enamine (Nitro ene hydrazine) structure, the C=C (1630–1660 cm^{-1}) and NO_2 (ν_s, 1250–1280 cm^{-1}) IR stretches are most diagnostic.[10b,10c] The dipolar (*aci*-nitronate) structure is characterized by the strong C=N (1590–1605 cm^{-1}) and N—O (1215–1260 and 1120–1180 cm^{-1}) stretches[10d] also observed in α-keto nitronate salts.[10e]

To examine the generality of the cycloaddition construction (Scheme II), we also wanted to have access to synthons of the type II (Scheme III) where n = 5 and 7. Thus, 2-nitrocycloheptane[6c] was transformed into its dimethylhydrazone 3 in excellent yield. However, we could not obtain a pure sample of 2-nitrocyclopentanone[6d] and had to directly derivatize the crude product to afford the hydrazone 2 in quantities sufficient only for trial alkylations, (Scheme V). The hydrazones 2 and 3 existed also exclusively in the *aci*-nitro form.

2. Dianion Generation and Alkylation. Following various precedents in the literature, primarily the work of Corey and Enders[7b] on the formation of dimethylhydrazone monoanions, we surveyed ca. 20 different

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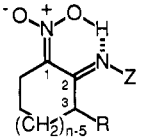
Table II. Selected Spectroscopic Data for 1–6, 16, and 17[a]



compd	n	Z	IR, cm^{-1} C=NO$_2$	^{1}H NMR, δ OH	^{13}C NMR, δ C(1)	^{13}C NMR, δ C(2)	Δδ, C(2)[b]
1	6	NMe_2	1592	11.24	116.4	159.0	
4a	6	NMe_2	1591	11.31	115.8	163.0	4.0
4b	6	NMe_2	1591	11.28	116.3	161.6	2.6
4c	6	NMe_2	1598	11.57	117.2	162.8	3.8
4d	6	NMe_2	1591	11.35	115.9	163.0	4.0
4e	6	NMe_2	1590	11.31	116.3	163.2	4.2
2	5	NMe_2	1626	9.38	117.2	161.9	
5a	5	NMe_2	1623	9.40	116.4	165.4	3.5
3	7	NMe_2	1587	11.76	120.6	164.8	
6a	7	NMe_2	1582	12.21	120.6	167.8	3.0
16	6	C_6H_{11}	1592	11.53	117.2	158.1	
17a	6	C_6H_{11}	1593	11.66	116.7	162.3	4.2
17b	6	C_6H_{11}	1593	11.54	117.1	160.9	2.8
17c	6	C_6H_{11}	1593	11.90	117.7	162.8	4.7
17d	6	C_6H_{11}	1593	11.70	116.9	162.3	4.2

[a] See the Experimental Section for complete data. [b] Positive numbers indicate downfield shifts.

base/solvent combinations for efficient dianion generation and alkylation. As test electrophiles we used either methyl iodide or (*E*)-1-iodo-4-hexene. The results of these studies can be summarized as follows: (1) 1 equiv of NaH or KH in combination with *n*-BuLi, LDA, or KHMDS gave poor yields (25%) of alkylation product and recovered educt, (2) 2 equiv of LDA or KHMDS gave similar results as in 1, (3) 1 equiv of KH in combination with *sec*-BuLi gave ca. 50% of alkylation product, (4) 2 equiv of *sec*-BuLi gave the best results (>80%), (5) HMPA (5 equiv based on hydrazone) was essential for deprotonation *and* alkylation, and (6) alkyl *iodides* must be used; best yields are obtained with 1.4–2.0 equiv.

The final protocol, which was found to be generally applicable for different nitro hydrazones and electrophiles, was as follows: deprotonation at −78 °C for 3 h with 2.1 equiv of *sec*-BuLi in THF/HMPA (5 equiv), cooling to −95 °C, adding alkyl iodide (1.4 equiv), and warming to −78 °C (30 min) and then to −10 °C to quench. All electrophiles were consumed below −40 °C.

The results of alkylation of **1** by use of this protocol are collected in Table I, entries 1–5. As we had hoped, the nitro hydrazones were considerably more nucleophilic than the nitro ketones as their respective dianions. Thus, in addition to reacting readily with methyl and allyl electrophiles, **1** also underwent clean displacements at primary and *secondary* centers. The crude products obtained by simple aqueous workup and evaporation were >90% pure by 300-MHz ^{1}H NMR analysis and could be directly purified by crystallization. The crude product from entry 3 was always contaminated with **1** (from competing elimination) and had to be chromatographed. We found the alkylation to respond well to scale up as the reaction in entry 5 could be run on a scale to produce 5.8 g of **4e** (80% yield) after one recrystallization.

The dianions of nitro hydrohydrazones **2** and **3** were generated in similar fashion except that *t*-BuLi had to be used as base to avoid addition to the hydrazone function. These species were alkylated only with methyl iodide. The product **5a** was obtained cleanly as a yellow solid, which could be recrystallized as in the cyclohexyl series. The alkylation of **3**, however, was more difficult since it was prone to addition of the alkyllithium bases (even *t*-BuLi added in 10% yield). The product **6a** was an oil, which required chromatography and distillation.

All of the alkylated nitro hydrazones except **6a** existed exclusively in the *aci*-nitro form as was readily apparent from their IR and NMR spectra (Table II). In addition, both epimeric nitro forms of **6a** were detected in a ratio of 70/23/7 = *aci*/nitro a/nitro b. While the alkylations proved to be high yielding and selective, the regiochemistry of dianion formation and alkylation was far from assured (α to hydrazone or α to nitro? See Discussion). Furthermore, inspection of the spectroscopic data did not allow an unambiguous assignment. The most suggestive information came from comparison of the changes in the ^{13}C resonances for C(1) and C(2) in the **1–3** to **4–6** transformation (Table II). The ^{1}H NMR and IR data show clearly that these compounds all exist exclusively or predominantly in the *aci*-nitro form. Thus, the assignment of the C(1) and C(2) resonances is simple. Upon substitution, the chemical shift of C(2) moves downfield by 2.6–4.0 ppm while that of C(1) changes only ±0.8. This is most consistent with the substitution of H for alkyl at C(3). The β- and γ-shielding effects for carbonyl-type carbons are much smaller than for hydrocarbons but are nonetheless well documented to be ca. +2 ppm (β) and −1 ppm (γ).[11] Similar comparisons will be made in the product nitroalkenes. The ultimate proof of regiochemistry comes from the successful intramolecular cycloaddition of **10e**.[1b]

3. Transformation to Nitroalkenes. Reduction. With a general access to substituted nitro hydrazones, we focused our efforts on converting **4–6** into nitroalkenes. The most direct route entailed reduction to a nitro hydrazine and elimination, by analogy to the nitro ketone to nitroolefin transformation reported by Zajac.[4n] Whereas dialkylhydrazones are resistant to reduction with $NaBH_4$ (and have been used as protecting groups in this capacity[12]), the nitro hydrazones **4** and **5** were reduced extremely rapidly in ethanol with that reagent (Table III). As ex-

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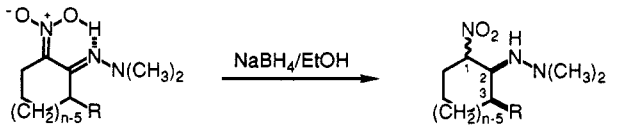
Table III. Sodium Borohydride Reduction of Nitro Hydrazones 4-6



4-6 7-9

compd	temp, °C	time, h	product[a]	yield,[b] %
1	0	0.5	7	94[c]
4a	0	0.5	**7a**	90
4b	0	0.5	**7b**	93
4c	20	2.0	**7c**	90
4d	0	1.0	**7d**	94
4e	0	0.5	**7e**	100[d]
5a	0	3.0	**8a**	93
6a	20	15	**9a**	63

[a] Usually a mixture of two to three isomers (see text for explanation). [b] Yield of all isomers combined after chromatography. [c] Up to 5% of nitroalkene **10** formed upon reduction. [d] Crude yield.

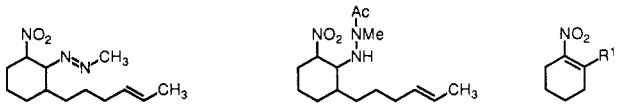
Table IV. Selected ^{1}H NMR Data for 7a and 7e

	chemical shift, δ		coupling constant (J), Hz			
compd	HC(1)	HC(2)	(1,6$_{ax}$)	(1,6$_{eq}$)	(1,2)	(2,3)
7a(major)	4.58	3.38	4.4	8.4	7.8	4.1
7a(minor)	4.19	3.68	12.5	2.7	2.7	*a*
7e(major)	4.67	3.44	5.8	5.7	6.1	4.3
7e(minor)	4.13	3.78	12.6	2.7	2.7	*a*

[a] HC(2) is a broad singlet.

pected,[13] hydrazone **6** required 15 h at room temperature to be reduced by $NaBH_4$. The remarkable facility of reduction must arise from the activation provided by intramolecular protonation from the nitronic acid. Having interrupted the conjugation between dimethylamino and *aci*-nitro substituents, the compounds **7–9** all exist in the normal, nitro form. As a consequence, two or three epimers of each hydrazine were usually produced, which were purified and characterized as a mixture of isomers. In most cases, one isomer dominated the mixture and could be assigned a unique structure by ^{1}H NMR spectroscopy. Two cases were examined carefully, and the relevant ^{1}H NMR data for the assignment of stereostructure are collected in Table IV. In **7a**, three components could be detected by TLC and ^{1}H NMR of which one was present in greater than 90%. From homonuclear decoupling experiments, the vicinal coupling constants could be extracted for two of the three components. In the major isomer HC(1) appeared as a triplet of doublets with $J_t \approx$ 4 Hz, while HC(2) was a doublet of doublets $J_d \approx 4$ and 8 Hz. The absence of a large (>10 Hz) coupling rules out any diaxial relationships with these protons. This pattern is most consistent with a trans diaxial relationship of the nitro and hydrazine groups and with the methyl occupying an equatorial position. The magnitude of the couplings to both protons on C(6) is in line with an axial nitro group.[6e] Similarly, in **7e**, no large couplings are observed. The fact that the difference between the vicinal couplings is smaller is also precedented in the observations of Zajac[6e] on conformationally mobile systems. In both **7a** and **7c**, a minor isomer was detected, which displayed a diagnostic doublet of triplets for HC(1) with J_d = 12.5 Hz. Since large couplings were absent from HC(2), this is most consistent with the structure epimeric at C(1) only. Thus, the stereoselectivity in reduction of the hydrazone is high. It was not established if the configuration at C(1) represented the product of kinetic control.[14]

Elimination. The surprising and pleasant facility of reduction of the nitro hydrazones was surpassed by the surprising and unpleasant recalcitrance of the nitro hydrazines to undergo elimination! In the absence of any direct precedent, we began the study by applying those methods that had been successful in the dehydration of β-nitro alcohols, using **7e** as the test substrate (Table V). The hydrazines were strikingly resistant to direct elimination (strong acid or base) or functionalization. Attempts to sulfonylate the internal nitrogen of the hydrazine were entirely unsuccessful. Treatment of **7e** with mesyl chloride or triflic anhydride with or without added base led to either no reaction or many products by TLC (entries 1–3). More encouraging were the results on treatment of **7e** with DCC in the presence of copper(I) chloride,[4k] entries 4 and 5. The reaction worked well on a small scale, but upon scale up the major product was an interesting azo compound, **13**.



13 14 R^1 = sBu:**18** R^1 = tBu:**19**

Apparently copper(I) chloride oxidized the hydrazine with concomitant demethylation leaving behind reduced copper metal.[15] Other carbodiimides and Lewis acid catalysts also failed. Attempts to liberate the dimethylhydrazine unit by forming stable hydrazones with acetone, 2,2-dimethoxypropane, or formaldehyde under a variety of conditions were also unsuccessful (entries 6–8). Acylation of the internal nitrogen of **7e** also proved difficult as it was recovered unchanged from refluxing trifluoroacetic anhydride (entry 9). Ultimately, acetic anhydride was found to give good yields of **10e**, but only under the specified conditions of high temperature and short reaction time (entries 10–13). Prolonged reaction times at lower temperatures gave significant amounts of terminally acetylated product **14**, which was resistant to further reaction either in situ or upon separate treatment with base. In most cases *N*-(dimethylamino)acetamide could be recovered from the reaction mixtures.

While the elimination conditions are admittedly harsh, the nitroalkenes did survive this treatment as shown by the generally good yield obtained from the various nitro hydrazines (Table VI). The only exception is **11a**, which suffered considerable decomposition during the reaction (entry 7). The nitroalkenes **10–12** displayed the same downfield shift of C(2) in their ^{13}C NMR spectra[11b] further supporting the assignment of regiochemistry (Table VII).

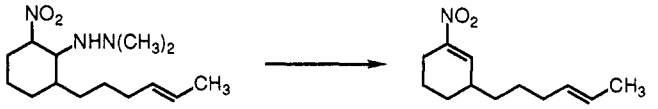
In an attempt to streamline the alkylation–reduction–elimination sequence, we briefly examined the nitro tri-

(13) Brown, H. C.; Ichikawa, K. *Tetrahedron* **1957**, *1*, 221.

(14) Zimmerman first demonstrated the production of axial nitro compounds by kinetic protonation of nitronates. Zimmerman, H. E.; Nevins, T. E. *J. Am. Chem. Soc.* **1957**, *79*, 6559.

(15) Copper (I) oxidation of *N,N'*-dialkylhydrazines is known. Chen, S. G.; Zand, R.; Steel, C. *J. Am. Chem. Soc.* **1961**, *83*, 2895.

Table V. Elimination Conditions To Form Nitroalkene 10e

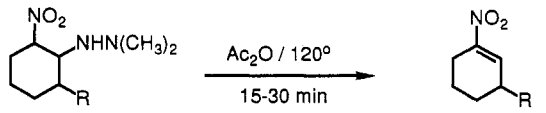


7e 10e

entry	strategy	conditions	yield, 10e, %	comments
1	sulfonamide formation	MsCl/neat/70 °C	trace	
2		$MsCl/(CH_2Cl)_2/DBU/70$ °C		NR
3		$(CF_3SO_2)_2O/DMAP/20$ °C		mostly educt
4	guanidine formation	DCC/CuCl/DMF	81	20-mg scale
5		DCC/CuCl/DMF	16	(100-mg scale) major product 13
6	hydrazone formation	acetone/HOAc/20 °C		NR
7		$Me_2C(OMe)_2$/HOAc/20 °C		many products
8		formalin/10% HOAc/20 °C	trace	many products
9	acethydrazide formation	$(CF_3CO)_2O$/neat/reflux		NR
10		$(CH_3CO)_2O/20$ °C/1.5 h		many products
11		$(CH_3CO)_2O/45$ °C/4 h	40	60% 14[a]
12		$(CH_3CO)_2O/60$ °C	67	33% 14[a]
13		$(CH_3CO)_2O/120$ °C/15 min	73	4.0-g scale

[a] By integration of ^1H NMR signals in mixture.

Table VI. Preparation of Nitroalkenes 10–12



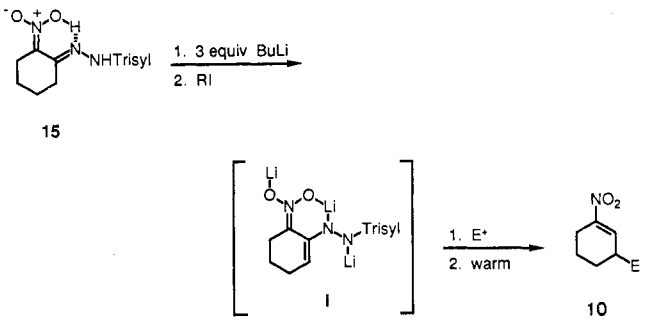
entry	compd	R	product	yield, %
1	7	H	10	50
2	7a	CH_3	10a	72
3	7b	CH_2=$CHCH_2$	10b	72
4	7c	$(CH_3)_2CH$	10c	69
5	7d	$CH_3(CH_2)_3$	10d	71
6	7e	CH_3CH=$CH(CH_2)_3$	10e	73
7	8a	CH_3	11a	35
8	9a	CH_3	12a	55

sylhydrazone 15 (Scheme VI). By analogy to the generation of β-keto ester tosylhydrazone *trianions* by Fuchs,[16] we envisaged forming species i, which after alkylation and Shapiro fragmentation[17] should lead directly to 10. The trisylhydrazone 15 proved rather unstable and decomposed upon chromatography, recrystallization, or treatment with acid or base. With 3.1 equiv of *sec*-BuLi, the typical orange color developed, which discharged upon addition of methyl iodide, but no tractable products could ever be isolated after various quenching protocols.

C. α-Nitro Imines. The successful studies with α-nitro hydrazones described above encouraged us to examine the chemistry of α-nitro imines. In particular, we hoped to find in these derivatives a milder reduction–elimination procedure. Feuer has described the preparation of α-nitro keto imines by propyl nitrate nitration of cycloalkanone *tert*-butylimines[6a,10d] in 35–50% yields. For our study we elected to use α-nitro ketones in hope of realizing improved overall yields. Furthermore, Feuer[10d] has also demonstrated that bromination of α-nitro imines in basic media (presumably via monoanions) occurs at C(3). This, together with the close analogy to metalloenamine chemistry,[8c] provided ample precedent for the alkylation step.

1. 2-(Cyclohexylimino)-1-nitrocyclohexane (16). The cyclohexylimine 16 had been reported previously,[18]

Scheme VI



15 I 10

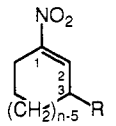
so we followed the described procedure. Thus, combining 2-nitrocyclohexanone and cyclohexylamine in ethyl acetate and heating to reflux for 30 min provided a yellow solid, mp 128–130 °C, as described. However, elemental and spectroscopic analysis showed this material to be the ammonium nitrate salt! Moreover, if more than 1 equiv of cyclohexylamine was used, a good yield of *N*-cyclohexyl-6-nitrohexanamide was obtained. The desired product was ultimately secured (65% yield) by adaption of the method used for the α-nitro hydrazones with use of the cyclohexylammonium acetate (benzene/18 h/20 °C). The yellow, crystalline (mp 115 °C) cyclohexylimine, like its *tert*-butyl congener,[10d] existed completely in the *aci*-nitro form (Table II). The preparation of the corresponding *tert*-butylimine was unacceptably sluggish by this method, providing <3% conversion after 30 h at reflux.

2. Dianion Generation and Alkylation. Applying the optimal deprotonation/alkylation protocol established for the hydrazones (section B.2), we were able to isolate the alkylated α-nitro imines, 17, in acceptable yields (Table VIII). In all cases, the product of addition of *sec*-BuLi 18 also was isolated in ca. 10% yield. Remarkably, switching to *t*-BuLi did not suppress this side reaction as the corresponding *tert*-butyl adduct 19 could be isolated in similar yields. The alkylated products, 17, existed also in the *aci*-nitro form and displayed the expected shieldings in their ^{13}C NMR spectra for substitution at C(3) (Table II).

3. Transformation to Nitroalkenes. Following our own experience, direct reduction of α-nitro imine 17b with sodium borohydride in ethanol proceeded rapidly at 0 °C. We were delighted to discover that under these conditions

(16) Bunnell, C. A. Fuchs, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 5184.
(17) (a) Shapiro, R. H. *Org. React. (N.Y.)* **1976**, *23*, 405. (b) Lipton, M. F.; Shapiro, R. H. *J. Org. Chem.* **1978**, *43*, 1409. (c) Nakai, T.; Mimura, T. *Chem. Lett.* **1980**, 931 and references cited therein.
(18) Bischoff, V. C.; Schroder, E. *J. Prakt. Chem.* **1972**, *314*, 891.

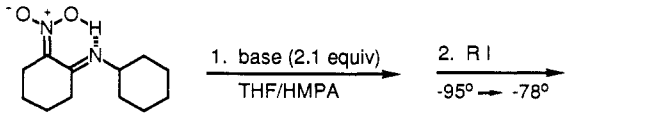
Table VII. Selected Spectroscopic Data for 10-12[a]



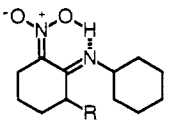
compd	n	^{1}H NMR, δ (J, Hz) HC(3)	^{13}C NMR, δ C(1)	C(2)	ΔδC(2)[b]
10	6	7.32 (4.0)	149.9	134.6	
10a	6	7.16 (s)	149.0	138.9	4.3
10b	6	7.22 (s)	149.5	137.0	2.4
10c	6	7.27 (s)	149.7	137.0	2.4
10d	6	7.22 (s)	149.1	137.9	3.3
10e	6	7.22 (s)	149.4	138.2	3.6
11a	5	6.88 (1.8)	152.1	142.9	
12a	7	7.17 (3.2)	153.6	143.4	

[a] For complete data see the Experimental Section. [b] Positive numbers indicate downfield shifts.

Table VIII. Alkylation of the Dianion from 16



16



17

entry	base	R	product[a]	yield,[b] %
1	*sec*-BuLi	CH_3	**17a**	68
2	*t*-BuLi	CH_3	**17a**	66
3	*sec*-BuLi	CH_2=$CHCH_2$	**17b**	70
4	*t*-BuLi	CH_2=$CHCH_2$	**17b**	62
5	*sec*-BuLi	$(CH_3)_2CH$	**17c**	54
6	*sec*-BuLi	$CH_3(CH_2)_3$	**17d**	60

[a] In all cases, either **18** or **19** was isolated in ca. 10% yield. [b] Yield after chromatography.

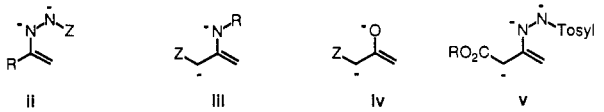
a *26% yield of nitroalkene **10b** was obtained.* This could be improved to 62% by using sodium borohydride in combination with cerium trichloride.[19] The best conversion to **10b** was achieved by adding 2.5 equiv of sodium borohydride in portions over 4 h (82%). *We have found the combination of $NaBH_4$ and $CeCl_3 \cdot 7H_2O$ to be a mild and general method for transforming α-nitro imines to nitroalkenes.* The results of this one-pot reduction–elimination are found in Table IX. In general, ethanol is the preferred solvent unless the α-nitro imine is very reactive in which case methanol is superior (entries 2, 9). Two equivalents each of cerium trichloride and sodium borohydride seem to be optimal. In sluggish reactions, best results were obtained by adding additional equivalents of both reagents over several hours. Heating was occasionally necessary to complete the eliminations. In the case of **17c**, the reduction was very slow. The nitroalkenes were obtained in 53–91% yield after chromatography with >98% purity by GC analysis.

The mildness and generality of the $NaBH_4/CeCl_3$ reduction–elimination of α-nitro imines prompted us to examine this reaction in the α-nitro hydrazones (Table IX, entries 10, 11). In entry 10, the hydrazone **1** was consumed within 4 h at 20 °C, but the elimination was considerably slower than in **16** (entry 1). Even after 2.5 h at reflux with excess cerium trichloride, 18% of the hydrazine **7** was isolated. Again, the difficulty of eliminating *N,N*-dimethylhydrazine foils this procedure. While it may be possible to use the $CeCl_3 \cdot 7H_2O$ to produce the nitroalkene from **7**, the mildness of reaction with **16** and **17** discouraged further studies.

A comparison of the overall efficiency of the two methods for the conversion of 2-nitrocyclohexanone to the 3-substituted nitrocyclohexene is constructed in Table X. The overall yields are modest, but it should be noted that the yields are for rigorously purified intermediates.

Discussion

A. Dianion Generation and Structure. The technique of generating polymetalated derivatives of functionalized organic molecules has been extensively developed[20] since the pioneering work of Hauser and Harris.[21] For the hydrazone functional group di- and even trianions have been generated, again following initial studies by the Hauser group.[22] These polyanions, however, have the general structure ii wherein Z = M, H, aryl, aryl SO_2 or



ii iii iv v

aryl CO. Thus, NH deprotonation constitutes one of the anions. The considerable body of literature on the Shapiro reaction[17] derives from the chemistry of these species (Z = aryl SO_2). In contrast, the dianions we have studied possess the general structure iii, which bears an obvious relationship to the 1,3-dianions, iv, studied by Hauser.[21] Analogous structures have been reported on only two previous occasions. In extending his work on β-dicarbonyl dianions, Hauser deprotonated and alkylated the phenylimine of acetylacetophenone (iii: Z = PhCO; R = Ph).[23] In a more related example, Fuchs[16,24] has reported the

(19) Stork has observed the direct reduction–elimination of nitro ketones with use of this reagent. Stork, G.; Clark, G.; Weller, T. *Tetrahedron Lett.* **1984**, *25*, 5367.

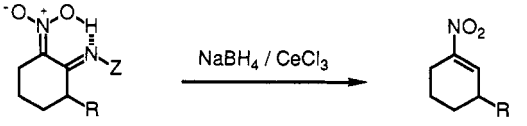
(20) (a) Kaiser, E. M.; Petty, J. D.; Knutson, P. L. A. *Synthesis* **1977**, 509. (b) Bates, R. B. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, I., Eds.; Elsevier: Amsterdam, 1980; Part A, Chapter 1. (c) Seebach, D.; Pohmakotr, M. *Tetrahedron* **1981**, *37*, 4047.

(21) (a) Hauser, C. R.; Harris, T. M. *J. Am. Chem. Soc.* **1958**, *80*, 6360. (b) Harris, T. M.; Harris, C. M. *Org. React. (N.Y.)* **1969**, *17*, 155.

(22) (a) Henoch, F. E.; Hampton, K. G.; Hauser, C. R. *J. Am. Chem. Soc.* **1967**, *89*, 463. (b) Beam, C. F.; Sandifer, R. M.; Foote, R. S.; Hauser, C. R. *Synth. Commun.* **1976**, *6*, 5. (c) Sandifer, R. M.; Davis, S. E.; Beam, C. F. *Ibid.* **1976**, *6*, 339.

(23) Boatman, S.; Hauser, C. R. *J. Org. Chem.* **1966**, *31*, 1785.

Table IX. One-Pot Reduction Elimination[a]

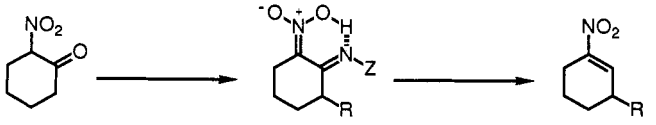


10

entry	compd	$NaBH_4$, equiv	$CeCl_3 \cdot 7H_2O$, equiv	time, h	temp, °C	product	yield,[b] %
1	**16**	1.5	1.2	2	20	**10**	75
2	**16**[c]	1.5	1.0	2	20	**10**	77
3	**17a**[c]	1.5	1.2	2	20	**10a**	69[d]
4	**17a**	2.0	2.0	4 (2)	20 (50)	**10a**	78
5	**17b**	2.5	0	1	20	**10b**	26
6	**17b**	2.0	3.0	8	20	**10b**	62
7	**17b**	2.5[e]	2.0	4	20	**10b**	82
8	**17c**	3.0	2.0	9 (12)	20 (50)	**10c**	53
9	**17d**[c]	1.5	1.2	1	20	**10d**	91
10	**1**	2.5	3.5	4	20	**10**[f]	15
11	**1**	2.5	3.5	25 (2.5)	20 (80)	**10**[g]	50

[a] All reactions were run in ethanol unless otherwise stated. [b] Yield after chromatography. [c] Reaction in methanol. [d] Amine still present. [e] 1.5 equiv of $NaBH_4$ added followed by another 1.0 equiv after 2 h. [f] Compound **7** was isolated in 36% yield. [g] Compound **7** was isolated in 10% yield.

Table X. Summary of the Yields of Transformations[a]



1 10

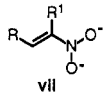
compd	Z	R	derivatization	alkylation	reduction	elimination	overall
10a	NMe_2	CH_3	79	86	90	72	44
10a	C_6H_{11}	CH_3	65	68	78		34
10b	NMe_2	$CH_2{=}CHCH_2$	79	81	93	72	43
10b	C_6H_{11}	$CH_3{=}CHCH_2$	65	70	82		37
10c	NMe_2	$(CH_3)_2CH$	79	72	90	69	35
10c	C_6H_{11}	$(CH_3)_2CH$	65	54	53		19
10d	NMe_2	$CH_3(CH_2)_3$	79	80	94	71	42
10d	C_6H_{11}	$CH_3(CH_2)_3$	65	60	91		35

[a] All yields (%) are given for purified (chromatographed, distilled, or crystallized) materials.

formation and trapping of β-keto ester tosylhydrazone trianions, v. These species are formed at −10 °C with 3 equiv of LDA and decompose to dienolates at 0 °C. From the trapping experiments, it appears that v was not generated stoichiometrically with LDA.

By comparison, there exists considerable precedent in the chemistry of polymetalated derivatives of nitro aliphatic compounds from the work of Seebach.[25] Both, α,α′-dianions, vi, and α,β-dianions (super enamines),[26] vii, have been generated with and without additional anion stabilizing groups. Since we were dealing with secondary

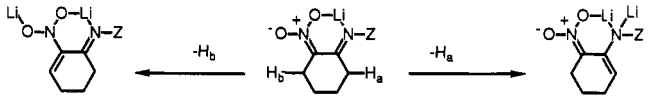
vi



vii

nitro compounds, only dianions of the type vii were possible. The α,β-dianion of nitrocyclohexane is generated at −90 °C with *n*-BuLi and *t*-BuLi in the presence of HMPA,[26a] conditions similar to ours. Thus, the question of gross dianion structure could be summarized (Scheme VII) in terms of the relative, kinetic acidifying effects of a hydrazone/imine ($-H_a$) to form ix or a nitronate ($-H_b$) to form x. *In all cases studied, the products arose from alkylation of the dianion ix exclusively.* At this time we cannot rule out partial formation of x since the documented instability of such species may account for lower yields with α-nitro imines.

Scheme VII



x viii ix

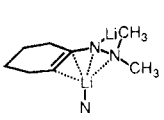
The detailed structure of the α-nitro hydrazone and α-nitro imine dianions ($2Li^+ \cdot 1^{2-}$, $2Li^+ \cdot 16^{2-}$) is the subject for future studies. Nonetheless, it is instructive at this point to speculate on reasonable possibilities based on the known structures of the isolated nitro, hydrazone, and imine anions. The structure of metalated hydrazones and imines derived from both ketones and aldehydes has been extensively investigated by the groups of Newcomb and

(24) See also: (a) Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 774. (b) Caille, J. C.; Bellamy, F.; Guilard, R. *Tetrahedron Lett.* **1984**, *25*, 2345.

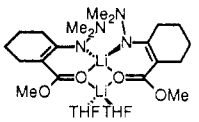
(25) (a) Seebach, D.; Lehr, F. *Helv. Chim. Acta* **1979**, *62*, 2239. (b) Seebach, D.; Lehr, F.; Gonnermann, J. *Ibid.* **1979**, *62*, 2258. (c) Seebach, D.; Eyer, M. *J. Am. Chem. Soc.* **1985**, *107*, 3601.

(26) (a) Brandli, U.; Eyer, M.; Seebach, D. *Chem. Ber.* **1986**, *119*, 575. (b) Seebach, D.; Henning, R.; Mukhopadhyay, T. *Ibid.* **1982**, *115*, 1705. (c) Seebach, D.; Henning, R.; Gonnermann, J. *Ibid.* **1979**, *112*, 234. (d) Seebach, D.; Henning, R.; Lehr, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 458.

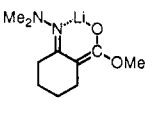
Bergbreiter,[8c] Enders,[7d] Fraser,[7c] Knorr,[27] and Meyers[28] by use of ^{1}H NMR spectroscopy. Direct observation of lithiohydrazones and lithioenamines coupled with stereochemical analysis of kinetic trapping experiments has provided a wealth of information on the carbon–carbon and carbon–nitrogen double bond geometries. These studies are primarily concerned with the origin of the "syn effect"[7c] and effects of deprotonation conditions on anion structure in acyclic and macrocyclic frameworks. In $2Li^+ \cdot 1^{2-}$ and $2Li^+ \cdot 16^{2-}$, the geometries of the carbon–carbon and carbon–nitrogen bonds are assured (E_{CC}/Z_{CN}, ix, Scheme VII) by both structural constraints and the observed syn disposition of the nitrogen substituent in the products. The more interesting question, which is not addressed in the ^{1}H NMR studies, is the location and role of the counterion and overall aggregation state. These questions have been addressed in elegant studies by Collum[29] using X-ray crystallography in conjunction with solution molecular weight determinations and reaction kinetics. The lithiated cyclohexanone dimethylhydrazone is tetrameric in solution with the lithium atom bound in an η^4-fashion to the π-system, xi.[29a] In contrast, the 2-carbomethoxy derivative is dimeric in solution (though readily dissociating) and has the expected chelation of the lithium atoms, xii.[29c] Furthermore, on the basis of bond lengths, Collum proposes a significant contribution from the resonance structure xiii. The analogy between xiii and the monoanions of 1 is unavoidable. Thus, we propose a hybrid, xiv, which embodies the salient features of both structure, as a reasonable representation of $2Li^+ \cdot 1^{2-}$.



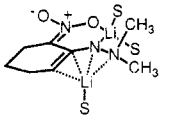
xi



xii

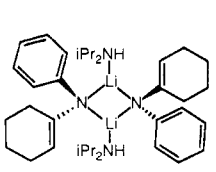


xiii

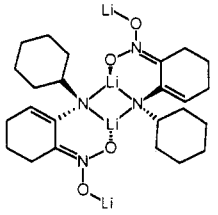


xiv

For the structure of $2Li^+ \cdot 16^{2-}$, we again cite the X-ray structure of lithiocyclohexanone phenylimine, which exists as a diisopropylamine solvated dimer,[29c] xv. Simply replacing the amine ligand with the internally coordinating nitronate group generates structure xvi. However, in



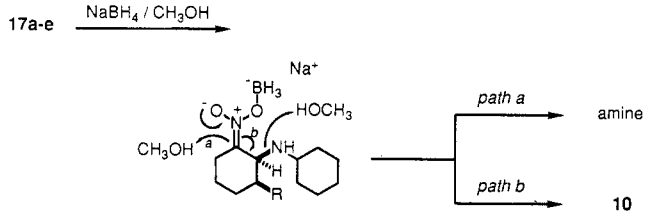
xv



xvi

neither of these structures, xiv nor xvi, is the nature of lithium–nitronate bonding taken in consideration. A recent X-ray crystal structure determination of α-(nitrobenzyl)lithium by Boche[30] revealed that this basic structural unit is an LiONOLiO six-membered ring made up of a nitronate, two lithium atoms, and an oxygen from a second nitronate. How this feature may be incorporated into the structure is at present unclear. The importance of these speculations becomes apparent in the design of *chirally modified* α-nitro hydrazones and imines for asymmetric alkylations.[31]

Scheme VIII



B. Reduction–Elimination. The extraordinary facility of reduction of α-nitro hydrazones 1 and 4–6 most certainly derives from the intramolecular activation through hydrogen bonding with the *aci*-nitro proton. This proposal is supported by the resistance of simple dimethylhydrazones to $NaBH_4$ reduction[12b] and by the observation that α-nitro tosylhydrazones, which exist in the nitro form, undergo *reductive denitration* with $LiAlH_4$.[10a] The cis stereoselectivity of the reduction of α-nitro hydrazones 4 is in contrast to the predominantly trans-selective reduction of 2-alkylcyclohexanones with $NaBH_4$.[32] However, this can be readily understood in terms of steric approach control.[32b] Since **4a–e** all exist in the *aci*-nitro form, the hydrazone is necessarily syn to the alkyl substituent (the "syn effect" notwithstanding). In order to avoid $A^{1,3}$ strain, the alkyl group must take up a pseudoaxial position.[33] Careful inspection of the HC(3) signals in the ^{1}H NMR spectra of **4a–e** revealed the absence of any large (>6 Hz) couplings, in agreement with the pseudoequatorial nature of this proton. Thus, approach of the borohydride ion is strongly shielded by the neighboring alkyl group, giving rise to predominantly cis isomers.

The difficulties encountered in functionalizing the α-nitro hydrazines at the internal nitrogen are related to the behavior of unsymmetrical hydrazines. In general, the disubstituted end of unsymmetrical hydrazines is the more nucleophilic,[34] and in this case the cyclohexyl substituent makes matters even worse, sterically. The isolation of 14 from lower temperature reactions with acetic anhydride suggests that the terminal nitrogen is competitively acylated. Therefore, the fate of the acylammonium intermediate (i.e., transacylation vs. demethylation) determines the success of the reaction. The resistance of 14 to elimination reinforces our notion that activation of the internal nitrogen is essential for elimination. Since the hydrazine group is axial in both isomers, there is no stereoelectronic problem in elimination, once the acylation has occurred.

The rapid reduction of α-nitro imines with $NaBH_4$, though certainly facilitated by intramolecular hydrogen

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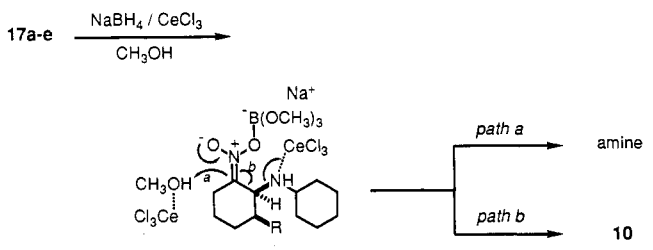
Scheme IX



bonding, is less surprising since the reduction of simple imines with $NaBH_4$[35] is known. However, the isolation of nitroalkene **10b** in 26% yield was unexpected on the basis of our experience with α-nitro hydrazones and the high yield reduction of nitro ketones to nitro alcohols described by Zajac.[4n] Since the amount of nitroalkene did not increase with extended reaction time, we imagined that elimination was occurring from a kinetically generated complex, which partitioned to the two products (Scheme VIII). From our recent work with cerium halide assisted organometallic additions to hydrazones[36] we chose to examine the Luche reagent ($NaBH_4/CeCl_3 \cdot 7H_2O$)[37] in hope of activating the product amine further by coordination to cerium(III). While this proved to be a successful strategy, the origin of the effect is still unclear. From careful studies of the mechanism of ketone reductions, Luche suggests that the special properties of this reagent derive from the Lewis acidity of the $CeCl_3$, which gives rise to the rapid formation of alkoxyborohydrides and to general-acid catalysis in the additions. Thus, the picture for reduction–elimination is slightly modified as shown in Scheme IX. We again suggest the formation of a complex that partitions in order to explain the spontaneous formation of nitroalkene upon reduction and rather sluggish elimination of the amine byproduct (Table IX, entry 8).

Finally, one curious fact merits comment. Despite the use of large excesses of borohydride (usually 8–12 reducing equiv), no reduction of the nitroalkenes was detected. This is very difficult to understand since sodium borohydride is the time-honored reagent of choice for the reduction of nitroalkenes to nitroalkanes.[38] Furthermore, Shechter[38a] has demonstrated that sodium trimethoxyborohydride is equally capable of this reduction.[39] The explanation of this observation may well be hidden in the peculiar nature of the Luche reagent, and this must await further mechanistic studies.

Conclusions

We have developed a general procedure for the preparation of 3-substituted nitrocycloalkenes starting with nitro ketones. The method works best for six- and seven-membered ring systems. The dianions of the α-nitro hydrazones and α-nitro imines are easily generated and highly reactive toward alkylation. Both α-nitro hydrazones and α-nitro imines can be transformed via reduction–elimination procedures to the nitroalkenes, thus demonstrating their potential as nitroalkene d^3 synthons.[40] The advantages of this method are the (1) crystallinity of the intermediates, (2) generality of the construction, (3) mildness of unmasking procedures, and (4) overall compatibility with the olefin functions desired for intramolecular cycloadditions. Perhaps the most important advantage of this over existing methods[4] is the potential for asymmetric synthesis via chiral, nonracemic hydrazones or imines. Efforts in our laboratories are already under way in this area, and the outcome will be the subject of future reports.[31]

Experimental Section

General Methods. ^1H NMR spectra were recorded on a General Electric QE-300 (300 MHz) instrument in deuteriochloroform. Proton NMR chemical shifts are given in ppm with chloroform (δ 7.26) as internal reference; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet), followed by a *J* (coupling constant) given in hertz. Broadened (br) is indicated where appropriate. Data are presented in the form: chemical shift (multiplicity, coupling constant, integrated intensity, assignment). ^{13}C NMR spectra were recorded on the QE-300 (75.5 MHz) instrument. Carbon NMR shifts are given in ppm with deuteriochloroform (δ 77.07) as the internal reference. Infrared spectra (IR) were obtained from an IBM FT IR-32 spectrometer in carbon tetrachloride solutions. Peaks are reported in cm^{-1} with s, m, and w corresponding to strong (66–100%), medium (33–66%), and weak (0–33%), respectively. Mass spectra were recorded on a Varian MAT CH-5 spectrometer with ionization voltages of 10 and 70 eV. Data are recorded in the form *m/z* (intensity relative to base = 100). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory. Melting points (mp) were determined with a Thomas-Hoover capillary melting point apparatus and are corrected. Solids that decomposed upon heating are indicated by dec. Bulb-to-bulb distillations were done with a Büchi GRK-50 Kugelrohr apparatus. Boiling points (bp) refer to air-bath temperature and are uncorrected. Analytical TLC was performed on Merck silica gel 60 plates with QF-254 indicator. Visualization was accomplished with UV light, iodine, 2,4-DNP, or phosphomolybdic acid. R_f data refer to solvent mixtures of hexane and EtOAc (hexane/EtOAc). Silica gel column chromatography was performed by the method of Still[41] (32–63-μm silica gel, Woelm). *sec*-Butyllithium and *tert*-butyllithium were purchased from Aldrich and freshly titrated by the method of Gilman[42] and with diphenylacetic acid, respectively. Air- or water-sensitive reactions were performed in oven- (140 °C) and/or flame-dried glassware under a dry N_2 atmosphere. Saturated aqueous sodium chloride is referred to as brine. Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents: hexane ($CaCl_2$), ether ($CaSO_4/FeSO_4$), ethyl acetate (K_2CO_3), dichloromethane ($CaCl_2$).

Starting Materials. The following reagents were prepared by literature methods: 1-acetoxycyclopentene,[43a] 1-acetoxycyclohexene,[43b] 1-acetoxycycloheptene,[43c] 2-nitrocyclopentanone,[6d] 2-nitrocyclohexanone,[6c] 2-nitrocycloheptanone,[6c] (*E*)-1-iodo-4-hexene.[44]

Nitro Hydrazone Preparations. (*E*)-2-(Dimethylhydrazono)-1-*aci*-nitrocyclohexane (1). A 250-mL, three-necked, round-bottomed flask fitted with a 50-mL addition funnel, gas inlet, and thermometer was charged with 50 mL of benzene and 4.45 mL (59 mmol, 1.2 equiv) of *N,N*-dimethylhydrazine. Glacial acetic acid (3.35 mL, 59 mmol, 1.2 equiv) was added

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(39) Spectroscopic evidence (^{11}B NMR) for the intermediacy of methoxyborohydrides in $NaBH_4$ reduction of nitroalkenes has been provided by Kabalka.[38f]
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dropwise via the addition funnel, under nitrogen while a temperature < 10 °C was maintained. The addition funnel was rinsed with a few milliliters of benzene and charged with a solution of 2-nitrocyclohexanone (7.0 g, 49 mmol) in 43 mL of benzene. The solution was added dropwise at 4–6 °C over 30 min, and the final mixture was allowed to warm to room temperature. After 1 h at room temperature, the biphasic mixture was poured into saturated $NaHCO_3$ solution (200 mL) and extracted with ethyl acetate (4 × 150 mL). The individual organic extracts were washed with water (1 × 200 mL) and brine (1 × 200 mL), and the aqueous washes were back-extracted with ethyl acetate (1 × 100 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and evaporated to leave yellow crystals. Recrystallization of the crude product from ether (35 mL) provided 6.59 g (73%) of **1**: mp 86.5–87.5 °C; ^1H NMR (300 MHz) δ 11.24 (s, 1 H, NOH), 2.66 (br s, 2 H), 2.54 (br s, 8 H, HC(3), HC(6), and $N(CH_3)_2$), 1.59 (br s, 4 H, HC(4) and HC(5)); ^{13}C NMR (75.5 MHz) δ 159.0 (C(2)), 116.4 (C(1)), 48.0 ($N(CH_3)_2$), 26.0, 25.3, 21.9, 21.1; IR 2992 w, 2950 s, 2865 m, 2828 w, 2784 w, 1592 s, 1476 s, 1449 s, 1429 m, 1410 s, 1375 s, 1350 s, 1320 s, 1264 m, 1246 m, 1202 s, 1159 m, 1113 s, 1076 s, 1026 m, 1015 m, 980 w, 911 m; MS (70 eV), m/z 185 (M^+, 15), 168 (20), 137 (21), 96 (14), 95 (11), 82 (12), 59 (11), 55 (16), 44 (100); TLC R_f 0.35 (hexane/EtOAc, 1/2). Anal. Calcd for $C_8H_{15}N_3O_2$: C, 51.88; H, 8.16; N, 22.69. Found: C, 51.89; H, 8.35; N, 22.58.

(*E*)-2-(Dimethylhydrazono)-1-*aci*-nitrocyclopentane (2). Concentrated nitric acid (2.14 mL, 34.08 mmol) was added to a solution of 1-acetoxycyclopentene (4.3 g, 34.08 mmol) in acetic anhydride (10.3 mL, 109 mmol) at 0 °C. After the mixture was stirred for 2 h, the volatiles were removed at low pressure (5 mbar) at room temperature. The remaining red oil was diluted with benzene, and the solution was concentrated in vacuo. This sequence was repeated four times and afforded 3.37 g of the crude material. The crude nitro ketone (3 g, 23.2 mmol) in 5 mL of benzene was added slowly to a solution of *N,N*-dimethylhydrazine (2.12 mL, 27.9 mmol) and glacial acetic acid (1.6 mL, 27.9 mmol) in 15 mL of benzene at 7 °C. After being stirred for 1 day, the resulting black solution was concentrated in vacuo and chromatographed on silica gel (hexane/EtOAc, 1/1). Washing of the crystals with ethyl acetate afforded 300 mg (<5%) of the desired compound **2**: mp 148 °C dec; ^1H NMR (300 MHz) δ 9.38 (s, 1 H, HON), 2.89–2.65 (m, 4 H, $H_2C(5)$ and $H_2C(3)$), 2.61 (s, 6 H, $(H_3C)_2N$), 1.94–1.84 (m, 2 H, $H_2C(4)$); ^{13}C NMR (75.5 MHz) δ 161.91 (C(2)), 117.16 (C(1)), 48.21 (2 C, $(CH_3)_2N$), 31.11, 28.88, 18.17; IR 2961 w, 2928 w, 1626 m, 1472 w, 1437 w, 1425 w, 1387 m, 1213 w, 1124 w; MS (10 eV), m/z 171 (M^+, 80), 155 (11), 154 (100), 137 (22), 136 (13), 111 (17), 68 (19), 59 (20); TLC R_f 0.29 (hexane/EtOAc, 1/1). Anal. Calcd for $C_7H_{13}N_3O_2$ (171.19): C, 49.11; H, 7.65; N, 24.54. Found: C, 49.18; H, 7.73; N, 24.78.

(*E*)-2-(Dimethylhydrazono)-1-*aci*-nitrocycloheptane (3). To a magnetically stirred solution of *N,N*-dimethylhydrazine (0.58 mL, 7.63 mmol) in 10 mL of benzene was added glacial acetic acid (0.436 mL, 7.63 mmol) slowly at 10 °C. 2-Nitrocycloheptanone (1g, 6.36 mmol) in 4 mL of benzene was added at the same temperature, and the mixture was stirred for 3 h at room temperature. The reaction mixture was poured into 40 mL of water, and the aqueous solution was extracted with dichloromethane (3 × 30 mL) and washed with 1% $NaHCO_3$ solution (40 mL), water (40 mL), and brine (40 mL). The aqueous washes were back-extracted with dichloromethane (40 mL), dried over sodium sulfate, filtered, and concentrated. Recrystallization from isopropyl ether afforded 1.07 g (85%) of **3**: mp 95 °C; ^1H NMR (300 MHz) δ 11.76 (br s, 1 H, HON), 2.98–2.69 (m, 4 H, $H_2C(3)$ and $H_2C(7)$), 2.62 (s, 6 H, $(H_3C)_2N$), 1.73–1.54 (m, 6 H); ^{13}C NMR (75.5 MHz) δ 164.81 (C(2)), 120.64 (C(1)), 48.13 (2 C, $(CH_3)_2N$), 30.70, 27.39, 27.07, 26.05, 25.19; IR 2992 m, 2959 m, 2930 s, 2856 m, 1587 s, 1552 m, 1452 m, 1421 s, 1367 s, 1348 s, 1277 m, 1244 m, 1211 m, 1192 s, 1143 s, 1122 s, 1066 m, 1041 m, 1011 m, 956 s; MS (10 eV), m/z 200 (5), 199 (M^+, 53), 182 (34), 153 (62), 151 (31), 137 (13), 110 (28), 109 (19), 96 (11), 95 (11), 84 (39), 81 (11), 71 (24), 69 (26), 67 (14), 59 (35), 58 (10), 55 (13), 44 (20), 43 (100); TLC R_f 0.46 (hexane/EtOAc, 1/1). Anal. Calcd for $C_9H_{17}N_3O_2$ (199.25): C, 54.25; H, 8.60; N, 21.09. Found: C, 54.22; H, 8.54; N, 21.17.

Nitro Hydrazone Dianion Alkylations. General Procedure. To a magnetically stirred solution of the nitro hydrazone (**1–3**) in THF (5 mL/mmol of hydrazone) in a three-necked, round-bottomed flask fitted with thermometer, septum, and gas inlet tube was added dropwise HMPA (5 mmol/mmol of hydrazone), and the solution was cooled to −78 °C. *sec*-BuLi or *t*-BuLi (2.1 mmol/mmol of hydrazone) was added dropwise, and a yellow solution formed, which turned orange-red as the addition continued. After being stirred for 3 h, the mixture was cooled to −95 °C, and the alkyl iodide (1.4–1.8 mmol/mmol of hydrazone) was added neat. Five minutes after complete addition, the mixture was warmed to −78 °C, stirred for 30 min, and then allowed to warm slowly to −10 °C. The resulting gold reaction mixture was poured into 1% aqueous acetic acid (4 mL/mmol of hydrazone), extracted with dichloromethane (3 × 10 ml/mmol of hydrazone), washed with water and brine (1 × 10 mL/mmol of hydrazone), back-extracted with dichloromethane (1 × 10 mL/mmol of hydrazone), dried over sodium sulfate, filtered, and evaporated. Recrystallization from isopropyl ether afforded pure material. Compound **6a** was chromatographed on silica gel (hexane/EtOAc, 5/1) and bulb-to-bulb distilled.

(*E*)-2-(Dimethylhydrazono)-3-methyl-1-*aci*-nitrocyclohexane (4a): yield 462 mg (86%, after chromatography); mp 97 °C; ^1H NMR (300 MHz) δ 11.31 (s, 1 H, HON), 3.29–3.24 (m, 1 H, HC(3)), 2.77–2.68 (dt, 1 H, $H_aC(6)$), 2.62 (s, 6 H, $(H_3C)_2N$), 2.53–2.41 (m, 1 H, $H_bC(6)$), 1.76–1.56 (m, 4 H, $H_2C(5)$ and $H_2C(4)$), 1.26 (d, J = 7.0, 3 H, $H_3C(1')$); ^{13}C NMR (75.5 MHz) δ 163.01 (C(2)), 115.79 (C(1)), 48.54 (2 $C(CH_3)_2N$), 29.15 (C(3)), 28.30, 25.19, 19.67 (C(1')), 16.59; IR 2949 m, 2862 m, 2828 w, 2785 w, 1653 w, 1591 s, 1477 m, 1450 m, 1427 w, 1379 s, 1363 m, 1354 m, 1338 m, 1315 m, 1242 w, 1207 m, 1180 m, 1157 m, 1111 s, 1101 m, 1072 m, 1037 m, 1022 w, 989 w, 922 w. MS (10 eV), m/z 199.1 (M^+, 28), 182 (40), 165 (11), 151 (13), 137 (10), 110 (13), 95 (13), 81 (10), 67 (19), 59 (17), 55 (20), 44 (100), 42 (29); TLC R_f 0.56 (hexane/EtOAc, 1/2). Anal. Calcd for $C_9H_{17}N_3O_2$ (199.25): C, 54.25; H, 8.60; N, 21.09. Found: C, 54.27; H, 8.61; N, 21.06.

(*E*)-2-(Dimethylhydrazono)-3-(2-propenyl)-1-*aci*-nitrocyclohexane (4b): yield 493 mg (81% after recrystallization); mp 95–96 °C; ^1H NMR (300 MHz) δ 11.28 (s, 1 H, HON), 5.83–5.71 (m, 1 H, HC(2')), 5.12–5.07 (m, 2 H, $H_2C(3')$), 3.20–3.17 (m, 1 H, HC(3)), 2.77–2.69 (m, 1 H, $H_aC(6)$), 2.63 (s, 6 H, $(H_3C)_2N$), 2.56–2.41 (m, 2 H, $H_bC(6)$ and $H_aC(1')$), 2.26–2.15 (m, 1 H, $H_bC(1')$), 1.84–1.41 (m, 4 H, $H_2C(4)$ and $H_2C(5)$); ^{13}C NMR (75.5 MHz) δ 161.60 (C(2)), 135.42 (C(2')), 117.08 (C(3')), 116.33 (C(1)), 48.57 (2 C, $(CH_3)_2N$), 36.86, 33.92 (C(3)), 24.98, 23.38, 16.22; IR 2949 w, 2862 w, 2828 w, 1591 s, 1558 w, 1479 w, 1450 m, 1377 m, 1354 w, 1340 m, 1306 w, 1240 w, 1203 m, 1184 w, 1157 w, 1107 m, 1028 w, 1007 w, 918 w; MS (10 eV), m/z 226 (18), 225 (M^+, 57), 208 (58), 195 (18), 180 (13), 179 (99), 178 (17), 165 (15), 150 (16), 137 (50), 136 (47), 135 (19), 134 (33), 109 (13), 95 (17), 84 (41), 81 (11), 70 (10), 59 (16), 46 (14), 45 (29), 44 (100); TLC R_f 0.25 (hexane/EtOAc, 3/1). Anal. Calcd for $C_{11}H_{19}N_3O_2$ (225.28): C, 58.64; H, 8.50; N, 18.65. Found: C, 58.60; H, 8.55; N, 18.74.

(*E*)-2-(Dimethylhydrazono)-3-(1-methylethyl)-1-*aci*-nitrocyclohexane (4c): yield 439 mg (72% after chromatography); mp 90 °C; ^1H NMR (300 MHz) δ 11.57 (s, 1 H, HON), 3.13–3.08 (m, 1 H, HC(3)), 2.84–2.74 (dt, J = 16.8 and 7.7, 1 H, $H_aC(6)$), 2.60 (s, 6 H, $(H_3C)_2N$), 2.56–2.46 (ddd, J = 17.7, 7.0 and 5.0, 1 H, $H_bC(6)$), 2.10 (m, 1 H, HC(1')), 1.83–1.47 (m, 4 H, $H_2C(4)$ and $H_2C(5)$), 0.99 (d, J = 6.9, 3 H, $H_3C_a(2')$), 0.92 (d, J = 6.9, 3 H, $H_3C_b(2')$); ^{13}C NMR (75.5 MHz) δ 162.82 (C(2)), 117.14 (C(1)), 48.44 (2 C, $(CH_3)_2N$), 39.42 (C(3)), 30.24 (C(1')), 24.12, 22.72, 20.82 ($C_a(2')$), 19.06 ($C_b(2')$), 17.80; IR 2961 m, 2864 m, 2828 w, 1598 s, 1475 w, 1450 m, 1427 w, 1375 m, 1334 w, 1294 w, 1240 w, 1209 m, 1115 m, 1078 w, 1016 w, 983 w; MS (70 eV), m/z 227 (M^+, 19), 210 (29), 181 (20), 150 (10), 138 (15), 137 (19), 96 (10), 95 (14), 86 (13), 67 (12), 59 (11), 55 (17), 45 (12), 44 (100); TLC R_f 0.49 (hexane/EtOAc, 1/2). Anal. Calcd for $C_{11}H_{21}N_3O_2$ (227.30): C, 58.12; H, 9.31; N, 18.49. Found: C, 57.98; H, 9.39; N, 18.48.

(*E*)-2-(Dimethylhydrazono)-3-*n*-butyl-1-*aci*-nitrocyclohexane (4d): yield 523 mg (80% after recrystallization); mp 109–110 °C; ^1H NMR (300 MHz) δ 11.35 (s, 1 H, HON), 3.11–3.07 (m, 1 H, HC(3)), 2.76–2.67 (m, 1 H, $H_aC(6)$), 2.62 (s, 6 H, $(H_3C)_2N$), 2.62–2.44 (m, 1 H, $H_bC(6)$), 1.82–1.3 (m, 10 H), 0.95–0.90 (t, J = 6.8, 3 H, $H_3C(4')$); ^{13}C NMR (75.5 MHz) δ 163.00 (C(2)), 115.85 (C(1)), 48.33 (2 C, $(CH_3)_2N$), 33.92 (C(3)), 31.76, 29.13, 24.95, 23.26, 22.02, 16.33, 13.58 (C(4')); IR 2957 m, 2862 w, 1591 s, 1558 w, 1475 w, 1450 w, 1377 m, 1354 w, 1340 w, 1203 m, 1182 w, 1157 w, 1105 m; MS (10 eV), m/z 242 (15), 241 (M^+, 100), 225 (13), 224 (84),

195 (65), 193 (11), 152 (21), 151 (14), 138 (12), 137 (26), 96 (12), 59 (28), 45 (14), 44 (81); TLC R_f 0.29 (hexane/EtOAc, 3/1). Anal. Calcd for $C_{12}H_{23}N_3O_2$ (241.32): C, 59.72; H, 9.60; N, 17.41. Found: C, 59.50; H, 9.68; N, 17.34.

(*E*)-2-(Dimethylhydrazono)-3-[(*E*)-4-hexenyl]-1-*aci*-nitrocyclohexane (4e). Carbon NMR analysis of **4e** established olefin homogeneity at greater than 98% *E*: yield 473 mg (84% after chromatography); ^{1}H NMR (300 MHz) δ 11.31 (s, 1 H, NOH), 5.42 (m, 2 H, HC(4′) and HC(5′)), 3.08 (br s, 1 H, HC(3)), 2.74–2.48 (m, 4 H, HC(3′) and HC(6)), 2.60 (s, 6 H, $N(CH_3)_2$), 2.00 (m, 2 H), 1.80–1.37 (m, 7 H), 1.63 (d, J = 4.1, 3 H, CH_3); ^{13}C NMR (75.5 MHz) δ 163.21 (C(2)), 130.76, 125.35 (C(4′), C(5′)), 116.28 (C(1)), 48.69 ($N(CH_3)_2$), 34.29 (C(3)), 32.16 (C(6)), 31.91 (C(3′)), 27.22, 25.21, 23.61, 17.92 (C(6′)), 16.61; IR (CCl_4) 2992 m, 2948 s, 2861 s, 2828 m, 2783 m, 1590 s, 1476 s, 1449 s, 1375 s, 1352 s, 1240 m, 1208 s, 1183 s, 1157 m, 1109 s, 1013 m, 967 m, 899 m, 860 m; MS (70 eV), m/z 267 (M^+, 5), 221 (15), 178 (10), 122 (10), 96 (16), 95 (19), 94 (11), 85 (14), 82 (10), 81 (30), 79 (13), 72 (14), 69 (37), 68 (17), 67 (25), 60 (22), 59 (64), 58 (11), 57 (34), 55 (57), 54 (12), 53 (12), 45 (14), 44 (100, NMe_2), 43 (22), 42 (24), 41 (62), 39 (15); TLC R_f 0.29 (hexane/EtOAc, 3/1). Anal. Calcd for $C_{14}H_{25}N_3O_2$: C, 62.89; H, 9.42; N, 15.72. Found: C, 62.76; H, 9.50; N, 15.58.

(*E*)-2-(Dimethylhydrazono)-3-methyl-*aci*-nitrocyclopentane (5a): yield 210 mg (86%, after chromatography); mp 140.5 °C dec; ^{1}H NMR (300 MHz) δ 9.40 (s, 1 H, HON), 3.28–3.23 (m, 1 H, HC(3)), 2.93–2.74 (m, 2 H, $H_2C(5)$), 2.63 (s, 6 H, $(H_3C)_2N$), 2.10–2.02 (m, 1 H, HC(4)), 1.28 (d, J = 7.1, 3 H, $H_3C(1')$); ^{13}C NMR (75.5 MHz) δ 165.40 (C(2)), 116.40 (C(1)), 48.53 (2 C, $(CH_3)_2N$), 38.33 (C(3)), 27.21, 26.85, 18.79 (C(1′)); IR 2994 w, 2962 w, 2866 w, 1623 s, 1472 m, 1450 w, 1426 m, 1387 m, 1312 w, 1267 w, 1253 w, 1219 m, 1193 w, 1156 w, 1097 w; MS (10 eV), m/z 186 (6.5), 185 (M^+, 60), 169 (10), 168 (100), 151 (29), 150 (20), 82 (13), 60 (11), 59 (14), 55 (24), 43 (84); TLC R_f 0.45 (hexane/EtOAc, 1/1). Anal. Calcd for $C_8H_{15}N_3O_2$ (185.22): C, 51.87; H, 8.16; N, 22.69. Found: C, 51.70; H, 8.09; N, 22.50.

(*E*)-2-(Dimethylhydrazono)-3-methyl-1-*aci*-nitrocycloheptane (6a): yield 290 mg (54% after bulb-to-bulb distillation); bp 75 °C (0.03 Torr); ^{1}H NMR (300 MHz) δ 12.21 (br s, 1 H, HON), 4.23–4.15 (m, 1 H, HC(3)), 3.62 (dd, J = 16 and 1.5, 1 H, $H_aC(7)$), 3.61 (dd, J = 15.8 and 2.3, 1 H, $H_bC(7)$), 2.64 (s, 6 H, $(H_3C)_2N$), 1.92–1.58 (m, 6 H, $H_2C(4)$, $H_2C(5)$, and $H_2C(6)$), 1.28 (d, J = 7.4, 3 H, $H_3C(1')$), plus two isomers in the nitro form (a) 6.20 (dd, J = 10.0 and 6.5, 1 H, HC(1)) and (b) 5.11 (dd, J = 11.5 and 2.4, 1 H, HC(1)); ^{13}C NMR (75.5 MHz) δ 167.83 (C(2)), 120.62 (C(1)), 48.74 (2 C, $(CH_3)_2N$), 30.90 (C(3)), 30.85, 26.22, 25.71, 23.92, 19.53 (C(1′)), plus two isomers in the nitro form (a) 84.90 (C1)) and (b) 81.27 (C(1)); IR 2934 w, 2860 w, 1582 w, 1549 m, 1452 w, 1371 w, 1354 w, 1198 w, 1118 w, 1086 w, 963 w; MS (70 eV), m/z 214 (1.5), 213 (M^+, 31), 168 (12), 167 (100), 151 (10), 124 (57), 107 (17), 84 (14), 83 (13), 82 (22), 81 (15), 79 (24), 71 (11), 70 (14), 58 (20), 55 (24); TLC R_f 0.57 (hexane/EtOAc, 1/1). Anal. Calcd for $C_{10}H_{19}N_3O_2$ (213.27): C, 56.31; H, 8.98; N, 19.70. Found: C, 56.54; H, 9.06; N, 19.46.

Reductions. General Procedure. To a cold (0 °C) solution of the alkylated nitro hydrazone (**4–6**) in ethanol (4 mL/mmol of hydrazone) was added sodium borohydride (1.2 mmol/mmol of hydrazone) as a solid. The reaction mixture was stirred for 30 min, allowed to warm to room temperature, and then quenched with 10% HOAc (2 mL/mmol of hydrazone) after 15 min. The reaction mixture was extracted with dichloromethane (3 × 10 mL/mmol of hydrazone), washed with water and brine (1 × 10 mL/mmol of hydrazone), back-extracted with dichloromethane (1 × 10 mL/mmol of hydrazone), dried (Na_2SO_4), filtered, and concentrated. Column chromatography (SiO_2; hexane/EtOAc, 4/1) afforded pure hydrazines (**7–9**). All isomers were combined and used as a mixture for the next step.

2-(*N′*,*N′*-Dimethylhydrazino)-3-methyl-1-nitrocyclohexane (7a): yield 401 mg (90% after column chromatography); ^{1}H NMR (300 MHz) δ 4.61–4.54 (td, J = 8.2 and 4.5, 1 H, HC(1)), 3.40–3.36 (dd, J = 7.3 and 4.2, 1 H, HC(2)), 2.37 (s, 6 H, $(H_3C)_2N$), 2.18–1.94 (m, 3 H, $H_2C(6)$ and HC(3)), 1.63–1.51 (m, 4 H, $H_2C(4)$ and $H_2C(5)$), 0.92 (d, 3 H, J = 4.3 $H_3C(1')$); ^{13}C NMR (75.5 MHz) δ 85.55 (C(1)), 59.30 (C(2)), 47.56 (2 C, $(CH_3)_2N$), 30.51 (C(3)), 29.21, 28.24, 19.31, 14.05 (C(1′)); IR 2949 s, 2872 m, 2858 m, 2772 m, 1551 s, 1458 m, 1377 m, 1215 w, 1163 w, 1115 w, 1016 w, 898 w, 879 w, 852 w; MS (70 eV), m/z 201 (M^+, 16), 154 (11), 60 (7), 59 (100); TLC R_f 0.40, 0.32 (major), 0.21 (hexane/EtOAc, 3/1).

2-(*N′*,*N′*-Dimethylhydrazino)-3-(2-propenyl)-1-nitrocyclohexane (7b): yield 423 mg (93% after column chromatography); ^{1}H NMR (300 MHz) δ 5.80–5.68 (m, 1 H, HC(2′)), 5.17–5.02 (m, 2 H, $H_2C(3')$), 4.72–4.66 (dd, 1 H, J = 11.5 and 6.3, HC(1)), 3.51–3.48 (m, 1 H, HC(2)), 2.37 (s, 6 H, $(H_3C)_2N$), 2.22–1.86 (m, 5 H), 1.65–1.25 (m, 4 H, $H_2C(4)$ and $H_2C(5)$); ^{13}C NMR (75.5 MHz) δ 136.31 (C(2′)), 116.05 (C(3′)), 84.61 (C(1)), 57.57 (C(2)), 47.43 (2 C, $(CH_3)_2N$), 35.19 (C(3)), 33.35, 26.55, 25.42, 19.69; IR 2980 m, 2947 m, 2849 w, 2814 w, 2774 w, 1641 w, 1541 s, 1474 w, 1450 m, 1375 m, 1159 w, 1016 w, 995 w, 916 m, 850 w; MS–FI (8 kV), m/z 228 (16), 227 (M^+, 100); TLC R_f 0.63, 0.49 (major), 0.26 (hexane/EtOAc, 4/1).

2-(*N′*,*N′*-Dimethylhydrazino)-3-(1-methylethyl)-1-nitrocyclohexane (7c): yield 386 mg (90% after column chromatography); ^{1}H NMR (300 MHz) δ 5.0 (br s, 1 H, HC(1)), 3.77 (br s, 1 H, HC(2)), 2.43 (br s, 6 H, $(H_3C)_2N$), 2.1–1.89 (m, 2 H), 1.63–1.1 (m, 6 H), 0.97 (d, 3 H, $H_3C_a(2')$), 0.91 (d, 3 H, $H_3C_b(2')$); ^{13}C NMR (75.5 MHz) δ 83.11 (C(1)), 54.67 (C(2)), 47.56 (2 C, $(CH_3)_2N$), 42.14 (C(3)), 28.22 (C(1′)), 23.15, 22.71, 21.35 ($C_a(2')$), 21.21, 19.90 ($C_b(2')$); IR 2955 s, 2874 m, 2814 m, 2772 m, 1541 s, 1471 m, 1458 m, 1371 m, 1215 w, 1161 m, 1015 w, 906 w, 885 w, 854 w; MS–FI (8 kV) 229 (M^+), 195, 126; TLC R_f 0.75, 0.63 (major), 0.34 (hexane/EtOAc, 3/1).

2-(*N′*,*N′*-Dimethylhydrazino)-3-*n*-butyl-1-nitrocyclohexane (7d): yield 452 mg (94% after column chromatography); ^{1}H NMR (300 MHz) δ 4.70–4.64 (dd, J = 11.4 and 5.8, 1 H, HC(1)), 3.48–3.45 (br s, 1 H, HC(2)), 2.40 (s, 6 H, $(H_3C)_2N$), 2.25–2.0 (m, 2 H, $H_2C(6)$), 1.98–1.8 (m, 1 H, HC(3)), 1.7–1.5 (m, 10 H), 0.92–0.87 (t, 3 H, $H_3C(4')$); ^{13}C NMR (75.5 MHz) δ 84.76 (C(1)), 58.31 (C(2)), 47.50 (2 C, $(CH_3)_2N$), 35.62 (C(3)), 29.14, 28.46, 26.45, 25.85, 22.59, 19.93, 13.77 (C(4′)); IR 2951 s, 2860 s, 2814 m, 2772 m, 1543 s, 1458 m, 1375 m, 1159 w, 1014 w, 906 w, 852 w; MS–FI (8 kV), m/z 243 (M^+), 183; TLC R_f 0.54, 0.44 (major), 0.31 (hexane/EtOAc, 3/1).

(1*R,2*R**,3*R**)- and (1*R**,2*S**,3*S**)-2-(*N′*,*N′*-Dimethylhydrazino)-3-[(*E*)-4-hexenyl]-1-nitrocyclohexane (7e and 7e′):** yield 4.163 g (100%, crude) of a 91/9 mixture of **7e** and **7e′**; ^{1}H NMR (300 mHz) δ 5.40 (m, 2 H, HC(4′) and HC(5′)), 4.67 (q, J = 5.8, 0.91 H, **7e**-HC(1)), 4.13 (dt, J = 12.6 and 2.7, 0.09 H, **7e′**-HC(1)), 3.78 (br s, 0.09 H, **7e′**-HC(2)), 3.44 (dd, J = 4.3 and 6.1, 0.91 H, **7e**-HC(2)), 2.36 and 2.25 (2 s, 6 H, $N(CH_3)_2$), 2.14–1.80 (3 m, 6 H, HC(3), HC(6), and HC(3′)), 1.64 (d, J = 4.0, 3 H, CH_3), 1.60–1.18 (m, 8 H); IR 2940 s, 2857 m, 2815 m, 2772 w, 1541 s, 1458 m, 1375 m, 1157 w, 1015 w, 967 m, 909 w; TLC R_f 0.57 (**7e**) and 0.63 (**7e′**) (hexane/EtOAc, 3/1).

2-(*N′*,*N′*-Dimethylhydrazino)-3-methyl-1-nitrocyclopentane (8a): yield 173 mg (93% after column chromatography); ^{1}H NMR (300 MHz) major isomer δ 4.86–4.77 (m, 1 H, HC(1)), 3.72–3.68 (dd, J = 5.8 and 4.9, 1 H, HC(2)), 2.39 (s, 6 H, $(H_3C)_2N$), 2.37–2.31 (m, 1 H, HC(3)), 2.27–2.17 (m, 2 H, $H_2C(5)$), 2.07–1.95 (m, 1 H, $H_aC(4)$), 1.59–1.53 (m, 1 H, $H_bC(4)$), 0.95 (d, J = 7.2, 3 H, $H_3C(1')$); ^{13}C NMR (75.5 MHz) major isomer δ 90.43 (C(1)), 65.42 (C(2)), 47.43 (2 C, $(CH_3)_2N$), 35.92 (C(3)), 30.97, 29.07, 13.34 (C(1′)); IR 2955 m, 2874 w, 2845 w, 2814 w, 2772 w, 1549 s, 1460 w, 1373 w, 1109 w, 1016 w; MS (10 eV), m/z 187 (M^+, 9.4), 140 (9.7), 96 (5.5), 59 (94), 58 (27), 43 (22), 42 (100); TLC R_f 0.54, 0.4 (major), 0.21 (hexane/EtOAc, 5/2, 3× developed).

2-(*N′*,*N′*-Dimethylhydrazino)-3-methyl-1-nitrocycloheptane (9a): yield 245 mg (63% after column chromatography); ^{1}H NMR (300 MHz) 4.60 (dt, J = 6.1 and 5.9, 1 H, HC(1)), 3.50 (dd, J = 6.1 and 2.7, 1 H, HC(2)), 2.32 (s, 6 H, $(H_3C)_2N$), 2.14–2.08 (m, 3 H, $H_2C(7)$ and HC(3)), 1.8–1.3 (m, 6 H); ^{13}C NMR (75.5 MHz) δ 91.24 (C(1)), 62.61 (C(2)), 47.18 (2 C, $(CH_3)_2N$), 33.11 (C(3)), 31.75, 30.88, 27.48, 24.48, 17.90 (C(1′)); IR 2932 m, 2860 w, 2814 w, 2772 w, 1549 s, 1524 w, 1458 w, 1365 w, 1333 w, 1115 w, 1014 w, 891 w; MS (10 eV), m/z 215 (M^+, 9), 59 (100); TLC R_f 0.70, 0.63 (major), 0.5 (hexane/EtOAc, 1/1).

Eliminations. General Procedure. Acetic anhydride (25 mmol/mmol of hydrazine) was heated to 125 °C in a three-necked, round-bottomed flask fitted with an addition funnel and reflux condenser. The nitro hydrazine (**7–9**) was rapidly added neat. After 30 min, ethanol (2 mL/mmol of hydrazine) was added, and the solution was cooled to room temperature. The reaction mixture was poured onto half-saturated $NaHCO_3$ solution (10 mL/mmol of hydrazine), and the aqueous solution was extracted

with dichloromethane (3 × 10 mL/mmol of hydrazine) and washed with water and brine (1 × 10 mL/mmol of hydrazine). The aqueous washes were back-extracted with dichloromethane (1 × 10 mL/mmol of hydrazine), and the pooled extracts were dried over Na_2SO_4, filtered, and concentrated. Column chromatography (hexane/EtOAc, 15/1) and bulb-to-bulb distillation afforded pure nitroalkenes (**10–12**) as light yellow oils.

3-Methyl-1-nitrocyclohexene (10a): yield 195 mg (72% after distillation); bp 100–110 °C (0.1 Torr); ^{1}H NMR (300 MHz) δ 7.16 (s, 1 H, HC(2)), 2.65–2.44 (m, 3 H, H_2C(6) and HC(3)), 1.95–1.78 (m, 2 H, H_2C(5)), 1.71–1.57 (m, 1 H, H_aC(4)), 1.26–1.13 (m, 1 H, H_bC(4)), 1.14 (d, J = 7.1, 3 H, H_3C(1′)); ^{13}C NMR (75.5 MHz) δ 149.04 (C(1)), 138.92 (C(2)), 30.33 (C(3)), 29.17, 23.78, 20.54, 20.00 (C(1′)); IR 2945 m, 2865 m, 1668 w, 1653 w, 1558 m, 1522 s, 1456 m, 1435 m, 1361 m, 1340 s, 1132 w, 1014 w, 906 w; MS (70 eV), m/z 142 (1.5), 141 (M^+, 0.6), 111 (77), 95 (84), 79 (51), 67 (100); TLC R_f 0.5 (hexane/EtOAc, 3/1). Anal. Calcd for $C_7H_{11}NO_2$ (141.16): C, 59.56; H, 7.85; N, 9.92. Found: C, 59.25, H, 7.71, N, 10.07.

3-(2-Propenyl)-1-nitrocyclohexene (10b): yield 208 mg (72% after distillation); bp 120 °C (1 Torr); ^{1}H NMR (300 MHz) δ 7.22 (s, 1 H, HC(2)), 5.85–5.72 (m, 1 H, HC(2′)), 5.13–5.07 (m, 2 H, H_2C(3′)), 2.67–2.42 (m, 3 H, H_2C(6) and HC(3)), 2.23–2.18 (t, 2 H, H_2C(1′)), 1.98–1.77 (m, 2 H, H_2C(5)), 1.70–1.57 (m, 1 H, H_aC(4)), 1.32–1.20 (m, 1 H, H_bC(4)); ^{13}C NMR (75.5 MHz) δ 149.54 (C(1)), 137.01 (C(2)), 135.09 (C(2′)), 117.28 (C(3′)), 38.76 (C(3)), 35.21, 26.87, 23.92, 20.60; IR 3083 w, 2947 m, 2864 m, 1668 w, 1641 w, 1522 s, 1448 m, 1437 m, 1336 s, 1122 w, 993 m, 920 m; MS (10 eV), m/z 167 (M^+, 2), 150 (10), 137 (11), 126 (32), 125 (24), 121 (53), 120 (17), 110 (19), 108 (19), 96 (56), 95 (11), 94 (16), 93 (31), 92 (11), 91 (15), 81 (10), 80 (26), 79 (60), 78 (16), 68 (100), 67 (39); TLC R_f 0.7 (hexane/EtOAc, 3/1). Anal. Calcd for $C_9H_{13}NO_2$ (167.19): C, 64.65; H, 7.83; N, 8.37. Found: C, 64.36; H, 7.73; N, 8.47.

3-(1-Methylethyl)-1-nitrocyclohexene (10c): yield 165 mg (69% after distillation); bp 115 °C (0.1 Torr); ^{1}H NMR (300 MHz) δ 7.27 (s, 1 H, H(C2)), 2.69–2.60 (dm, J = 17.6, 1 H, H_aC(6)), 2.50–2.40 (m, 1 H, H_bC(6)), 2.27–2.21 (m, 1 H, HC(3)), 2.03–1.95 (m, 1 H, H_aC(4)), 1.84–1.72 (m, 2 H, H_2C(5)), 1.65–1.52 (m, 1 H, H_bC(4)), 1.34–1.22 (m, 1 H, HC(1′)), 0.97 (d, J = 4.2, 3 H, H_3C_a(2′)), 0.95 (d, J = 4.2, 3 H, H_3C_b(2′)); ^{13}C NMR (75.5 MHz) δ 149.75 (C(1)), 137.00 (C(2)), 42.01 (C(3)), 31.62 (C(1′)), 23.99, 23.77, 21.24, 19.51 (C_a(2′)), 19.43 (C_b(2′)); IR 2963 m, 2868 w, 1668 w, 1522 s, 1456 w, 1437 w, 1388 w, 1371 w, 1340 s, 1132 w, 1063 w, 833 w; MS (70 eV), m/z 169 (M^+, 0.7), 152 (10), 127 (77), 121 (21), 97 (100), 93 (15), 81 (37), 80 (14), 79 (41), 69 (28), 67 (26), 55 (17); TLC R_f 0.7 (hexane/EtOAc, 3/1). Anal. Calcd for $C_9H_{15}NO_2$ (169.21): C, 63.88; H, 8.93; N, 8.27. Found: C, 63.68; H, 9.10; N, 8.50.

3-*n*-Butyl-1-nitrocyclohexene (10d): yield 205 mg (71% after distillation); bp 100 °C (0.1 Torr); ^{1}H NMR (300 MHz) δ 7.22 (s, 1 H, HC(2)), 2.65–2.36 (m, 3 H, H_2C(6) and HC(3)), 1.95–1.76 (m, 2 H, H_2C(5)), 1.69–1.16 (m, 8 H), 0.91 (t, J = 6.9, 3 H, H_3C(4′)); ^{13}C NMR (75.5 MHz) 149.12 (C(1)), 137.90 (C(2)), 35.37 (C(3)), 34.31, 28.93, 27.06, 23.98, 22.51, 20.62, 13.72 (C(4′)); IR 2932 m, 2861 m, 1668 w, 1522 s, 1456 w, 1437 w, 1336 m, 1232 w, 1105 w; MS (10eV), m/z 183 (M^+, 23), 154 (15), 153 (97), 137 (11), 136 (28), 126 (14), 107 (41), 97 (81), 96 (12), 95 (75), 94 (21), 93 (33), 84 (16), 83 (21), 82 (14), 81 (100), 80 (13), 79 (38), 69 (33), 67 (48), 57 (32), 55 (44); TLC R_f 0.61 (hexane/EtOAc, 2/1). Anal. Calcd for $C_{10}H_{17}NO_2$ (183.24): C, 65.54; H, 9.35; N, 7.64. Found: C, 65.48; H, 9.33; N, 7.69.

3-[(*E*)-4-Hexenyl]-1-nitrocyclohexene (10e): yield 2.266 g (73% after column chromatography), 2.203 (71% after distillation); bp 100 °C (0.05 Torr); ^{1}H NMR (300 MHz) δ 7.22 (s, 1 H, HC(2), 5.41 (m, 2 H, HC=CH), 2.70–2.30 and 2.01–1.78 (2 m, 3 H and 4 H, respectively, HC(6), HC(3′), HC(3)), 1.65 (d, J = 4.7, 3 H, CH_3), 1.62–1.20 (m, 6 H); ^{13}C NMR (75.5 MHz) δ 149.39 (C(1)), 138.21 (C(2)), 130.74, 125.40 (C(4′), C(5′)), 35.55, 34.27, 32.49, 27.23, 26.87, 24.18, 20.84, 17.94; IR 2931 s, 2857 m, 1669 w, 1522 s, 1451 m, 1437 m, 1339 s, 1252 w, 1217 w, 1063 w, 1005 m, 968 m, 924 w; MS (10 eV), m/z 209 (M^+, 5), 192 (12), 162 (10), 161 (17), 153 (14), 140 (11), 139 (37), 135 (46), 133 (15), 127 (11), 123 (15), 122 (22), 121 (20), 119 (24), 109 (11), 107 (26), 105 (10), 97 (21), 95 (37), 94 (13), 93 (40), 92 (23), 91 (26), 82 (11), 81 (100), 80 (13), 79 (35), 69 (26), 68 (24), 67 (39), 57 (12), 55 (65); TLC R_f 0.45 (hexane/EtOAc, 15/1). Anal. Calcd for $C_{12}H_{19}NO_2$ (209.29): C, 68.87; H, 9.15; N, 6.69. Found: C, 68.82; H, 9.18; N, 6.68.

3-Methyl-1-nitrocyclopentene (11a): yield 57 mg (35% after column chromatography); bp 80 °C (0.5 Torr); ^{1}H NMR (300 MHz) δ 6.88 (d, J = 1.8, 1 H, HC(2)), 3.06–2.99 (m, 1 H, HC(3)), 2.98–2.75 (m, 2 H, H_2C(5)), 2.39–2.27 (m, 1 H, H_aC(4)), 1.71–1.61 (m, 1 H, H_bC(4)), 1.17 (d, J = 7, 3 H, H_3C(1′)); ^{13}C NMR (75.5 MHz) δ 152.14 (C(1)), 142.92 (C(2)), 38.54 (C(3)), 30.75, 29.13, 19.65 (C(1′)); IR 2966 m, 2932 m, 2872 m, 1642 w, 1549 w, 1518 s, 1460 m, 1377 w, 1358 s, 1340 m, 1306 w, 1109 w, 1014 w, 908 w, 885 w; MS (10 eV), m/z 127 (M^+, 6), 112 (4), 110 (13), 97 (85), 82 (20), 81 (100), 80 (51); TLC R_f 0.39 (hexane/EtOAc, 8/1). Anal. Calcd for $C_6H_9NO_2$ (127.13): C, 56.68; H, 7.13; N, 11.01. Found: C, 56.44; H, 7.29; N, 11.20.

3-Methyl-1-nitrocycloheptene (12a): yield 75 mg (55% after distillation); bp 50 °C (0.03 Torr); ^{1}H NMR (300 MHz) δ 7.17 (d, 1 H, J = 3.2, HC(2)), 3.12 (dd, 1 H, J = 16.3 and 6.2, H_aC(7)), 2.65–2.56 (m, 2 H, H_bC(7) and HC(3)), 1.98–1.40 (m, 6 H), 1.18 (d, 3 H, J = 7.2, H_3C(1′)); ^{13}C NMR (75.5 MHz) δ 153.55 (C(1)), 143.41 (C(2)), 33.79, 32.63 (C(3)), 29.10, 27.35, 24.67, 22.28 (C(1′)); IR 2965 w, 2930 m, 2876 w, 2854 w, 1665 w, 1524 s, 1458 w, 1444 w, 1383 w, 1369 w, 1332 s, 1218 w, 1157 w, 1097 w, 992 w, 864 w, 833 w; MS (10 eV), m/z 155 (M^+, 13), 125 (46), 109 (40), 108 (13), 107 (15), 93 (70), 91 (15), 81 (44), 80 (11), 79 (42), 69 (18), 67 (100), 57 (14), 55 (50), 42 (50); TLC R_f 0.7 (hexane/EtOAc, 3/1). Anal. Calcd for $C_8H_{13}NO_2$ (155.18): C, 61.91; H, 8.44; N, 9.02. Found: C, 62.08; H, 8.67; N, 8.99.

Nitro Imine Preparation. 2-(Cyclohexylimino)-1-*aci*-nitrocyclohexane (16). To a cold, magnetically stirred solution of cyclohexylamine (1.66 g, 16.77 mmol) in 60 mL of benzene was slowly added glacial acetic acid (0.958 mL, 16.77 mmol). To this white, pasty mixture was added a solution of 2-nitrocyclohexanone (2.0 g, 13.9 mmol) in 8 mL of benzene via an addition funnel. The cloudy, yellow solution was stirred for 18 h at room temperature. The resulting clear, yellow solution was poured into 40 mL of water acidified with 2 mL of 10% acetic acid. The aqueous solution was extracted with ethyl acetate (3 × 40 mL) and washed with water (1 × 40 mL) and brine (1 × 40 mL), and the aqueous washes were back-extracted with ethyl acetate (1 × 40 mL). The combined organic extracts were dried over sodium sulfate, filtered, and concentrated. The yellow oil, which solidified in vacuo, was recrystallized from isopropyl ether, and the mother liquor was chromatographed (EtOAc/hexane, 1/3) on silica gel. Total yield of **16**, 2.017 g (9 mmol, 65%): mp 114.5–115.5 °C; ^{1}H NMR (300 MHz) δ 11.53 (br s, 1 H, HON), 3.55–3.49 (m, 1 H, HC(1′)), 2.66 (br s, 2 H), 2.52 (br s, 2 H), 1.98–1.26 (m, 14 H); ^{13}C NMR (75.5 MHz) δ 158.09 (C(2)), 117.15 (C(1)), 51.14 (C(1′)), 32.91, 26.10, 25.31, 24.60, 23.78, 21.45, 20.94; IR 2938 s, 2859 m, 1592 s, 1448 m, 1433 m, 1415 m, 1377 s, 1353 s, 1341 m, 1326 m, 1214 s, 1189 m, 1145 m, 1124 s, 1072 m; MS (70 eV), m/z 225 (5), 224 (M^+, 37), 207 (20), 178 (10), 143 (26), 125 (15), 97 (51), 96 (10), 83 (10), 81 (11), 67 (20), 55 (37), 54 (12), 43 (20), 41 (37), 39 (10); TLC R_f 0.38 (EtOAc/hexane, 1/1). Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.25; H, 8.99; N, 12.49. Found: C, 64.31; H, 8.79; N, 12.38.

Nitro Imine Dianion Alkylation. General Procedure. To a magnetically stirred solution of **16** in THF (7 mL/mmol of **16**) in a three-necked, round-bottomed flask fitted with thermometer, septum, and gas inlet tube was added dropwise HMPA (5 mmol/mmol of **16**), and the solution was cooled to −78 °C. *sec*-BuLi (2.1 mmol/mmol of **16**) was added dropwise, and the clear, gold-yellow solution was stirred for 3 h at −78 °C and then cooled to −90 °C. The alkyl iodide (1.6 mmol/mmol of **16**) was added neat at −90 °C, and the solution was kept for 5 min at this temperature and stirred for 30 min at −78 °C, whereupon the solution turned orange. After a slow warm-up to −10 °C, the reaction mixture was poured into 1% acetic acid (11 mL/mmol of **16**), and the aqueous solution was extracted with dichloromethane (3 × 10 mL/mmol of **16**), and washed with water and brine (10 mL/mmol of **16**). The aqueous washes were back-extracted with dichloromethane (10 mL/mmol), dried over sodium sulfate, filtered, and concentrated. The resulting yellow liquid was chromatographed (EtOAc/hexane, 1/4) on silica gel and recrystallized from isopropyl ether. Yields are reported after chromatography.

2-(Cyclohexylimino)-3-methyl-1-*aci*-nitrocyclohexane (17a): yield 362 mg (68%); mp 133 °C; ^{1}H NMR (300 MHz) δ

11.66 (br s, 1 H, HON), 3.60–3.54 (m, 1 H, HC(1″)), 2.92–2.76 (m, 2 H, $H_2C(6)$), 2.58–2.47 (m, 1 H, HC(3)), 1.97–1.33 (m, 14 H), 1.26 (d, J = 7.1, 3 H, $H_3C(1')$); ^{13}C NMR (75.5 MHz) δ 162.27 (C(2)), 116.68 (C(1)), 51.32 (C(1″)), 34.68, 33.03, 29.00, 28.09, 25.28, 24.83, 24.30, 24.11, 19.52, 16.28; IR 2938 m, 2858 w, 1593 m, 1479 w, 1450 w, 1381 m, 1360 w, 1317 w, 1215 m, 1182 w, 1145 m, 1118 m, 1072 m; MS (10 eV), m/z 239 (10), 238 (M^+, 48), 221 (14), 208 (14), 203 (11), 192 (23), 157 (36), 111 (100), 110 (28); TLC R_f 0.38 (hexane/EtOAc, 5/3). Anal. Calcd for $C_{13}H_{22}N_2O_2$: C, 65.51; H, 9.31; N, 11.76. Found: C, 65.49; H, 9.29; N, 11.77.

2-(Cyclohexylimino)-3-(2-propenyl)-1-*aci*-nitrocyclohexane (17b): yield 142 mg (60%); mp 96 °C; ^1H NMR (300 MHz) δ 11.54 (br s, 1 H, HON), 5.73–5.67 (m, 1 H, HC(2′)), 5.08–5.03 (m, 2 H, $H_2C(3')$), 3.49–3.46 (m, 1 H, HC(1″)), 2.72–2.65 (m, 2 H, $H_2C(6)$), 2.51–2.39 (m, 1 H, HC(3)), 2.28–2.17 (m, 2 H, $H_2C(1')$), 1.89–1.22 (m, 14 H); ^{13}C NMR (75.5 MHz) δ 160.94 (C(2)), 134.40 (C(2′)), 117.64 (C(3′)), 117.14 (C(1)), 51.55 (C(1″)), 36.83, 34.72, 34.09 (C(3)), 32.89, 25.00, 24.83, 24.30, 24.15, 23.67, 16.01; IR 2938 m, 2857 w, 1593 m, 1450 w, 1379 m, 1358 w, 1226 w, 1211 w, 1190 w, 1145 w, 1120 m, 1072 w; MS (70 eV), m/z 265 (3), 264 (M^+, 16), 219 (15), 218 (70), 204 (28), 137 (27), 136 (100), 122 (13); TLC R_f 0.48 (hexane/EtOAc, 5/3). Anal. Calcd for $C_{15}H_{24}N_2O_2$: C, 68.15; H, 9.15; N, 10.60. Found: C, 68.01; H, 9.22; N, 10.62.

2-(Cyclohexylimino)-3-(1-methylethyl)-1-*aci*-nitrocyclohexane (17c): yield 323 mg (54%); mp 114 °C; ^1H NMR (300 MHz) δ 11.90 (br s, 1 H, HON), 3.57 (m, 1 H, HC(1″)), 2.91–2.80 (m, 1 H, HC(3)), 2.62–2.52 (m, 2 H, $H_2C(6)$), 1.98–1.24 (m, 15 H), 0.99 (2 d, 6 H, $H_3C_a(2')$ and $H_3C_b(2')$); ^{13}C NMR (75.5 MHz) δ 162.80 (C(2)), 117.71 (C(1)), 52.46 (C(1″)), 40.03 (C(3)), 35.04, 32.36, 30.29 (C(1′)), 24.90, 24.30, 24.16, 23.78, 23.22, 20.60 ($C_a(2')$), 19.60 ($C_b(2')$), 16.84; IR 2938 m, 2857 w, 1593 s, 1479 w, 1450 w, 1419 w, 1377 m, 1250 w, 1215 w, 1190 w, 1143 m, 1122 m, 1080 m; MS (10 eV), m/z 267 (8), 266 (M^+, 46), 249 (12), 236 (26), 224 (25), 220 (37), 185 (35), 179 (16), 178 (100), 139 (74), 138 (17), 97 (31), 96 (14); TLC R_f 0.41 (hexane/EtOAc, 5/3). Anal. Calcd for $C_{15}H_{26}N_2O_2$: C, 67.63; H, 9.84; N, 10.52. Found: C, 67.84; H, 10.00; N, 10.49.

2-(Cyclohexylimino)-3-*n*-butyl-1-*aci*-nitrocyclohexane (17d): yield 302 mg (60%); mp 88.5 °C; ^1H NMR (300 MHz) δ 11.70 (br s, 1 H, HON), 3.52–3.46 (m, 1 H, HC(1″)), 2.80–2.52 (m, 3 H, HC(3) and $H_2C(6)$), 1.97–1.26 (m, 20 H), 0.94 (t, J = 6.9, 3 H, $H_3C(4')$); ^{13}C NMR (75.5 MHz) δ 162.29 (C(2)), 116.92 (C(1)), 51.45 (C(1″)), 34.67, 34.27 (C(3)), 32.92, 31.79, 29.16, 25.09, 24.84, 24.35, 24.18, 23.39, 22.21, 16.16, 13.71 (C(4′)); IR 2938 m, 2859 m, 1593 s, 1468 w, 1450 m, 1419 w, 1379 s, 1358 m, 1250 w, 1221 w, 1209 w, 1190 m, 1145 m, 1121 m, 1072 m; MS (10 eV), m/z 281 (4), 280 (M^+, 22), 264 (1), 263 (6), 251 (1), 250 (6), 235 (5), 234 (24), 225 (4), 224 (27), 199 (7), 179 (14), 178 (100), 153 (26), 152 (15), 98 (5), 97 (22), 96 (9); TLC R_f 0.49 (hexane/EtOAc, 5/3). Anal. Calcd for $C_{16}H_{28}N_2O_2$: C, 68.53; H, 10.06; N, 9.99. Found: C, 68.41; H, 10.12; N, 9.97.

2-(1-Methylpropyl)-1-nitrocyclohexene (18): yield 33 mg (10%); ^1H NMR (300 MHz) δ 2.69–2.60 (m, 1 H, HC(1′)), 2.64–2.44 (m, 2 H), 2.18–2.06 (m, 2 H), 1.71–1.58 (m, 4 H, $H_2C(4)$ and $H_2C(5)$), 1.43–1.29 (m, 2 H, $H_2C(2')$), 1.06 (d, J = 5.6, 3 H, $H_3CC(1')$), 0.79 (t, J = 7.4, 3 H, $H_3C(3')$); ^{13}C NMR (75.5 MHz) δ 145.84, 141.50, 36.86 (C(1′)), 27.20, 26.96, 22.84, 22.18, 21.52, 18.39 ($CH_3C(1')$), 12.09 (C(3′)); IR 2965 m, 2936 m, 2867 w, 1539 w, 1520 s, 1457 w, 1452 w, 1440 w, 1362 w, 1350 w, 1120 w, 1091 w; TLC R_f 0.65 (hexane/EtOAc, 5/3).

Reduction–Elimination. General Procedure. To a magnetically stirred solution of the nitro imine (17) in ethanol (15 mL/mmol of 17) was added $CeCl_3 \cdot 7H_2O$ (2 mmol/mmol of 17) in one portion. Sodium borohydride (2 mmol/mmol of 17) was then added in small portions at room temperature, and the foamy mixture was stirred for 4 h. Nitro imines **17a** and **17c** were heated to 50 °C for 2 h and 12 h, respectively. After the indicated times, the reaction mixtures became white and milky and were quenched by the addition of acetone (4 mL/mmol of 17) and water (8 mL/mmol of 17). The milky solution was poured into water (40 mL/mmol of 17), and the aqueous solution was extracted with hexane (3 × 50 mL/mmol). The emulsions were dissolved with 10% acetic acid, and washed with half-saturated sodium bicarbonate solution, water, and brine (each 50 mL/mmol of 17). The aqueous washes were back-extracted with hexane (50 mL/mmol of 17), dried over sodium sulfate, filtered, and concentrated. Column chromatography (EtOAc/hexane, 1/15) afforded the desired nitroalkenes **10a–d**, which were shown to be identical with those obtained in the hydrazone sequence (^1H NMR, IR, GC purity >98%). The spectroscopic data from **10** was consistent with data reported in the literature.[4g]

Acknowledgment. We gratefully acknowledge the financial support provided for this project by the National Institutes of Health(Grant PHS GM-30938) and the Upjohn Co. This work was supported in part by the University of Illinois Mass Spectrometry Laboratory(Grant PHS HHS GM-27029).

Registry No. **1**, 112683-19-9; **2**, 112683-20-2; **3**, 112683-21-3; **4a**, 112683-22-4; **4b**, 112683-23-5; **4c**, 112683-24-6; **4d**, 112683-25-7; **4e**, 112683-26-8; **5a**, 112683-27-9; **6a**, 112683-28-0; **7**, 112683-30-4; **7a**, 112683-31-5; **7b**, 112683-32-6; **7c**, 112683-33-7; **7d**, 112683-34-8; **7e**, 112683-35-9; **7e′**, 112790-19-9; **8a**, 112683-36-0; **9a**, 112683-37-1; **10**, 2562-37-0; **10a**, 68216-48-8; **10b**, 112683-38-2; **10c**, 112683-39-3; **10d**, 112683-40-6; **10e**, 112683-41-7; **11a**, 112683-42-8; **12a**, 112683-43-9; **16**, 112683-44-0; **17a**, 112683-45-1; **17b**, 112683-46-2; **17c**, 112683-47-3; **17d**, 112683-48-4; **18**, 112683-49-5; **19**, 112683-50-8; $CH_2{=}CHCH_2I$, 556-56-9; $(CH_3)_2CHI$, 75-30-9; $CH_3(CH_2)_3I$, 542-69-8; (*E*)-$CH_3CH{=}CH(CH_2)_3I$, 112683-29-1; 2-nitrocyclohexanone, 4883-67-4; 1-acetoxycyclopentene, 933-06-2; 2-nitrocycloheptanone, 13154-27-3; 2-nitrocyclopentanone, 22498-31-3; cyclohexylamine, 108-91-8.

Peroxidation of *S*-(2-Methyl-2-propyl) 2-Methyl-2-propanesulfinothioate

Fillmore Freeman* and Choonsun Lee

Department of Chemistry, University of California, Irvine, Irvine, California 92717

Received March 27, 1987

Oxidation of 1 equiv of *S*-(2-methyl-2-propyl) 2-methyl-2-propanesulfinothioate (1) with 2 equiv of *m*-chloroperoxybenzoic acid (MCPBA) gives *S*-(2-methyl-2-propyl) 2-methyl-2-propanesulfonothioate (**4**, 13%), 2-methyl-2-propanesulfenic 2-methyl-2-propanesulfonic thioanhydride (**5**, 32%), 2-methyl-2-propyl 3-chlorobenzoate (**11**, 4%), 2-methyl-2-propyl 2-methyl-2-propanesulfinate (**12**, 22%), and small amounts of bis(2-methyl-2-propyl) trisulfide (**7**) and bis(2-methyl-2-propyl) tetrasulfide (**10**). Possible mechanisms for product formation are discussed.

Introduction

Although it is generally accepted that sulfinothioic acid *S*-esters, (thiosulfinates) are peroxidized to sulfonothioic acid *S*-esters (thiosulfonates), the peracid oxidation of *S*-(2-methyl-2-propyl) 2-methyl-2-propanesulfinothioate (1) may follow a different course. Freeman and Angeletakis[1,2] observed that the low-temperature *m*-chloroperoxybenzoic acid (MCPBA) oxidation of 1 led to diastereomeric *vic*-disulfoxides (α-disulfoxides, **2**, **3**).[1-5] Asakawa

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(2) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1983**, *105*, 4039.

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