respectively, of i-$C_3H_7NHCH_2OH$); only traces of other signals are seen in the spectrum. In a parallel experiment a sample which had stood in $CDCl_3$ at 25 °C for 18 h produced nearly identical spectra. Shift assignments were confirmed by examination of coupled spectra.

2,4,6,8-Tetrakis[2-(diphenylmethylsilyl)ethyl]-2,4,6,8-tetraazabicyclo[3.3.0]octane (11). To a suspension of 2-(diphenylmethylsilyl)ethylamine hydrochloride[12] (0.944 g, 3.6 mmol), anhydrous K_2CO_3 (1.00 g, 7.23 mmol), and freshly activated 4-Å molecular sieves (5 g) in ahydrous CH_3CN (30 mL) was added a solution of 40% aqueous glyoxal (0.128 g, 0.883 mmol) in ethanol (3 mL) with ice-bath cooling. Formaldehyde (0.143 g, 1.76 mmol of 37% aqueous solution) in CH_3CN (5 mL) was then added. After standing at 25 °C for 48 h, the mixture was filtered and the filtrate concentrated under reduced pressure to yield 0.41 g of an oil which was purified by chromatography on silica gel (elution with ethyl acetate/hexane) to yield 0.155 g (17%) of **11** as a colorless, viscous oil: ^1H NMR ($CDCl_3$) δ 7.15–7.50 (m, 40 H, C_6H_5), 3.83 (s, 2 H, ring CH), 3.49, 3.24 (AB q, J = 6.48 Hz, 4 H, ring CH_2), 2.5–2.71 (m, 8 H, CH_2CH_2Si), 1.10–1.31 (m, 8 H, CH_2CH_2Si), 0.49 (s, 12 H, CH_3). Anal. Calcd for $C_{64}H_{74}N_4Si_4$: C, 75.98; H, 7.37; N, 5.54. Found: C, 74.15; H, 7.22; N, 5.32. Like **1k**, compound **11** is decomposed by prolonged contact with silica gel.

1,1,2,2-Tetra-*N*-acetyl-1,1,2,2-tetra-*N*-benzyl-1,1,2,2-tetraaminoethane (8). 2,4,6,8-Tetrabenzyl-2,4,6,8-tetraazabicyclo-[3.3.0]octane (**1d**, 2.0 g, 4.21 mmol), acetic anhydride (100 mL), and 10% Pd/C catalyst (1.0 g) were shaken with hydrogen in a Parr apparatus (45 °C, 50 psi, 6 h). The catalyst was filtered off and the filtrate concentrated to remove volatiles, leaving an oil mixed with solid. The product was dissolved in CH_2Cl_2 (20 mL) and extracted twice with saturated $NaHCO_3$ solution, twice with 1 N HCl, and once with water. After drying with anhydrous $MgSO_4$, the CH_2Cl_2 solution was concentrated to dryness to yield an oil mixed with solid. Trituration with methanol (10 mL) and storage at 0 °C deposited crystalline **8**: 0.113 g, 4.3% yield; mp 175–177 °C; recrystallization from CH_3CN gave flat, rhombic prisms, mp 183–186 °C (42% recovery); ^1H NMR (DMSO-d_6) δ 7.4 (s, 20 H, C_6H_5), 6.5 (s, 2 H, CH), 4.8 (s, 8 H, CH_2), 2.0 (s, 12 H, CH_3). Anal. Calcd for $C_{38}H_{42}N_4O_4$: C, 73.76; H, 6.84, N, 9.06. Found: C, 74.55; H, 6.91; N, 8.73.

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Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, ^1H NMR and ^{13}C NMR spectra, and Figure S1 (molecular structure and numbering scheme) (12 pages); observed and calculated structure factors (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Dimethyldioxirane Oxidation of Primary Amines

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Several primary amines **2** have been oxidized with dimethyldioxirane (**1**) under a variety of conditions. Mixtures of dimeric nitrosoalkanes **4** and oximes **5** were typically obtained with solutions of the oxidant in excess. In several instances, nitrones **12** were found as byproducts in these reactions. In situ oxidations using oxone in buffered aqueous acetone solutions also gave nitrosoalkanes **4** and oximes **3** as important products; in addition, oxaziridines **11** were obtained in significant amounts in biphasic procedures containing methylene chloride. The corresponding nitroalkanes **5** were not formed in major amounts in either oxidation procedure, unless large excesses of oxidant were used. These results are discussed in terms of the several competing processes which occur under the different reaction conditions.

Although amines are readily oxidized by a range of reagents, there is a lack of general methodology for specific oxidative transformations of primary amines.[1] Soon after the introduction of dimethyldioxirane[2] (**1**) as a powerful but selective oxidant, its applications to this problem were examined. Several papers report efficient conversions of primary amines to the corresponding nitro compounds by this reagent, which can be either prepared and used separately or generated in situ.[3-7] Solutions of **1** have also been utilized for the controlled oxidation of amino sugars and esters of amino acids to the corresponding hydroxylamines.[8] Interestingly, complications associated with the nitroso compounds of intermediate oxidation state have not generally been a problem with this reagent, although nitroso dimers and oximes (common products with other oxidants[1,9]) were noted in a few instances.[5,6,8] Observations made during a study of the oxidation of allenic amines by **1**[10] suggested that this situation is not universal and prompted a study of primary amines bearing primary and secondary alkyl substituents. In these cases, tautomerization of the intermediate nitrosoalkanes to oximes is

(1) Rosenblatt, D. H.; Burrous, E. P. In *The Chemistry of Functional Groups: Supplement F. The Chemistry of Amino, Nitroso, Nitro Compounds and their Derivatives*; Patai, S., Ed.; Wiley Interscience: New York, 1982; p 1085.

(2) Curci, R. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1988; Vol. 2, Chapter 1. Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205.

(3) Murray, R. W.; Jeyaraman, R.; Mohan, L. *Tetrahedron Lett.* **1986**, *27*, 2335.

(4) Murray, R. W.; Rajadhyaksha, S. N.; Mohan, L. *J. Org. Chem.* **1989**, *54*, 5783.

(5) Zabrowski, D. L.; Noormann, A. E.; Kenneth, R. B. *Tetrahedron Lett.* **1988**, *28*, 4501.

(6) Eaton, P. E.; Wicks, G. E. *J. Org. Chem.* **1988**, *53*, 5353.

(7) For related oxidations of secondary amines, see: Murray, R. W.; Singh, M. *Tetrahedron Lett.* **1988**, *29*, 4677. Murray, R. W.; Singh, M. *Synth. Commun.* **1989**, *19*, 3509. Murray, R. E.; Singh, M. *J. Org. Chem.* **1990**, *55*, 2954.

(8) Wittman, M. D.; Malcohm, R. L.; Danishefsky, S. J. *J. Org. Chem.* **1990**, *55*, 1981. Galik, J.; Wong, H.; Krishnan, B.; Vyas, D. M.; Doyle, T. W. *Tetrahedron Lett.* **1991**, *32*, 1851.

(9) (a) Zajac, W. W.; Walters, T. R.; Woods, J. M. *Synthesis* **1988**, 808. (b) Zajac, W. W.; Walters, T. R.; Darcy, M. G. *J. Org. Chem.* **1988**, *53*, 5856. (c) Baer, H. H.; Lee Chiu, S. H. *Can. J. Chem.* **1973**, *51*, 1812. (d) Burckard, P.; Fleury, J.; Weiss, F. *Bull. Soc. Chim. Fr.* **1965**, *10*, 2730. (e) Robinson, C. H.; Milewach, L.; Hofer, P. *J. Org. Chem.* **1966**, *31*, 524. (f) Kahr, K.; Berther, C. *Chem. Ber.* **1960**, *93*, 132. (g) Sakaue, S.; Sakata, Y.; Nishiyama, Y.; Ishii, Y. *Chem. Lett.* **1992**, 289. (h) Gilbert, K. E.; Borden, W. T. *J. Org. Chem.* **1979**, *44*, 659. (i) Emmons, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 5528. (j) Keinan, E.; Mazur, Y. *J. Org. Chem.* **1977**, *42*, 844.

(10) Crandall, J. K.; Reix, T., manuscript in preparation.

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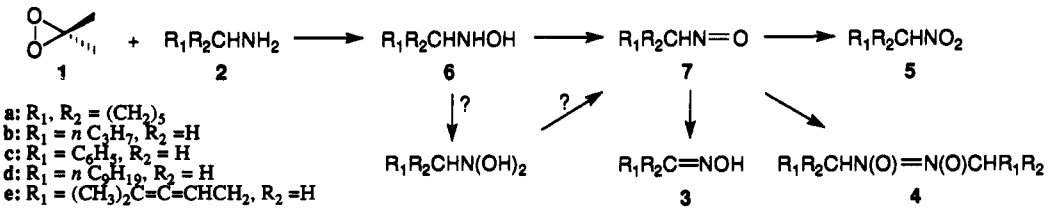
Scheme I



possible and dimerization is facilitated relative to the aryl and tertiary alkyl analogs that were intermediates in most of the reported examples using 1.[3-6]

The oxidation of cyclohexylamine (**2a**) by 1 was examined in some detail. Reactions were normally performed by adding an excess of the oxidant solution in several portions to a solution of **2a** until the starting amine was consumed, usually less than 0.5 h. A deep blue color suggestive of a nitroso compound was observed briefly upon mixing the reactants. Under these conditions the major products were oxime **3a** and the dimer of nitrosocyclohexane (**4a**); little nitrocyclohexane (**5a**) was found in the crude product mixtures. The relative amounts of **3a** and **4a** varied with the exact procedure, but dimer **4a** usually predominated over oxime **3a** and the total yields of chromatographically purified components were in the 60% range (Table I). The formation of **3a** and **4a** as major products is consistent with oxidations of primary amines with other reagents.[9] Since nitroso dimers are easily transformed to oximes by reaction with base,[11] it was possible to effect a preparative conversion of **2a** to oxime **3a** in 70% yield simply by heating the crude oxidation product with Et_3N in hexane prior to purification.

The sequence of reactions illustrated in Scheme I provides a basis for evaluation of these results. The starting amine is initially oxidized by 1 to a hydroxylamine derivative **6**, which is subsequently oxidized to a nitrosoalkane (**7**), perhaps via a dihydroxylamine intermediate. The final oxidation of the nitroso compound to a nitroalkane (**5**) is in competition with other reactions of **7**, namely dimerization to **4** and tautomerization to oxime **3**. These considerations suggested possible modifications of the reaction conditions in order to enhance the yield of the nitro compound. Thus, the addition of 7 equiv of 1 all at once to a solution of **2a** did give a mixture of dimer **4a** and nitro compound **5a** in about a 2:1 ratio. Likewise, the slow addition of a solution of **2a** to 10 equiv of 1 gave a comparable amount of nitroalkane, accompanied in this case by both **3a** and **4a**. While this demonstrates that competitive oxidation of the nitrosoalkane monomer **7** to nitro compound **5a** is possible, it is not feasible to use this procedure to obtain **5a** in good yield without employing an unreasonable excess of oxidant.

Several control experiments further substantiate the broad outlines of Scheme I. Independent oxidation of hydroxylamine **6a** gave a mixture of oxime **3a** and dimer **4a** as anticipated.[12] On the other hand, dimer **4a** reacted only slowly with the oxidant; 5 equiv of 1 for 6 h resulted in only 10% conversion to the nitro compound. This indicates that monomer–dimer equilibration is not facile under these conditions and rules out dimer **4a** as a significant source of **5a**. Oxime **3a** is also relatively unreactive to 1, although prolonged exposure results in significant degradation to cyclohexanone. This conversion may involve formation of *aci*-nitrocyclohexane (**8**) by oxygen transfer to the oxime nitrogen, followed by hydrolysis by the water invariably present in acetone solutions of 1.[13] A number of attempts to observe hydroxylamine **6a** in functioning oxidations of **2a** all failed. For example, reaction with only 1.2 equiv of 1 at −78 °C gave oxime **3a**, dimer **4a**, and starting material. This indicates that hydroxylamine **6a** is oxidized much more rapidly than the amine. Of particular significance for the work below was the accumulation of appreciable quantities of the cyclohexanimine of acetone (**9a**) in this particular reaction mixture (vide infra).

Table I. Oxidation of Primary Aliphatic Amines with 1

starting material	equiv of 1	other conditions	products[a] 3	4	5	other
2a	3.5		40%	21%	tr	
2a	5	$NaHCO_3$	21%	46%		
2a	5	K_2CO_3	25%	33%		
2a	7	CH_2Cl_2	20%	48%		
2a	10		24%	39%	tr	
2a	10	*b*	(10)	(50)	(40)	
2a	7	*c*		(60)	(40)	
2a	7	*c,d*		(70)	(30)	
2a	1.2	−78 °C	(39)	(16)	tr	**2a** (6), **9a** (39)
10	6.5			(90)	(10)	
10	6.5	H_2O[b]		(26)	(53)	**10** (21)
3a	5		(6)			(40)[e]
4a	5			(90)	(10)	
6a	2.5		(50)	(50)	tr	
2b	5		20%[f]	34%	g	**12b** 20%
2b	6	$NaHCO_3$	24%[f]	36%	tr	**12b** 15%
2b	6	K_2CO_3	16%[f]	58%	tr	
9b	4.5		(44)	(30)		**12b** (26)
2c	6	K_2CO_3	65%			
2c	6	$NaHCO_3$	69%			
2c	6		60%			
2d	6	K_2CO_3	73%[f]	18%	tr	
2d	6	$NaHCO_3$	43%[f]	13%	tr	**12d** (17)[h]
2d	6		51%[f]	18%	(8)	**12d** (3)[h]
2e	6	K_2CO_3	40%[f]	8%	g	
2e	6	$NaHCO_3$	36%[f]	9%	g	
2e	5		20%[f]	5%	g	**12e** 28%

[a] Percent indicates isolated yields; parentheses indicates percentage of crude product. [b] Amine added to 1. [c] 1 added in one portion. [d] Protected from light. [e] Cyclohexanone. [f] 3 and 4 isolated as a mixture. [g] Present as <5% of crude product. [h] Not isolated.

8 **10**

The suggestion that amine hydrochloride salts may be better starting materials than the amines themselves[4,6] spurred several experiments with cyclohexylammonium chloride (**10**). The addition of 7 equiv of 1 to **10** in acetone

(11) Di Giacomo, A. *J. Org. Chem.* **1965**, *30*, 2614.
(12) Tronchet, J. M.; Jean, E.; Galland-Barrera, G. *J. Chem. Res. Synop.* **1991**, 244.
(13) Peracids convert oximes to nitro compounds, presumably via *aci*-nitro compounds: Sundberg, R. J.; Burkowick, P. A. *J. Org. Chem.* **1968**, *33*, 4098. Olah, A.; Ramaiah, P.; Lee, C.-S.; Prakash, G. K. *Synlett.* **1992**, 337.

Table II. In Situ Oxidations of Amines with Oxone

starting material	equiv of oxone	cosolvent	products[a] 3	4	5	11
2a	4.5	CH_2Cl_2	10%	43%	10%	10%
2a	8	CH_2Cl_2	(12)	(60)	(14)	(14)
2a	16	CH_2Cl_2	(12)	(50)	(18)	(20)
2a	8		(2)	(26)	(72)	
2a	16			(14)	(86)	
2a	20			11%	65%	
9a	4.5			(5)	(22)	(73)
2b	4.5	CH_2Cl_2	24%[b]	30%	(6)	(27)
2b	4.5		40%[b]	40%	(12)	
2c	6	CH_2Cl_2	55%[b]			(38)[c]
2c	6		52%[b]			tr
2d	4.5	CH_2Cl_2	15%[b]	35%	(5)	37%
2d	4.5			64%	9%	(13)

[a] Percent indicates isolated yields; parentheses indicates percentage of crude product. [b] 3 and 4 were isolated as a mixture. [c] Not isolated.

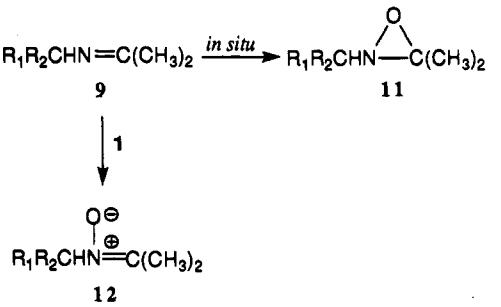
gave the usual predominance of dimer **4a**, along with nitro compound **5a** and lesser amounts of oxime **3a** in a slower, more complex reaction than with free **2a**. The addition of an acetone solution of salt **10** containing a small amount of water to 10 equiv of **1** did give the nitroalkane as the major product, but appreciable quantities of dimer **4a** and unreacted starting material were also present. Consequently, this approach to nitrocyclohexane was not pursued further.

Experimentation was also performed with in situ oxidations of **2a**, in which the amine was reacted with the $NaHCO_3$-buffered, aqueous acetone solutions of oxone (the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) normally used to generate **1** (see Table II). These oxidations most likely involve **1** as the active oxidant, since omitting the acetone results in slower, more random oxidations of **2a**. Nonetheless, the participation of caroate (peroxy monosulfate; HSO_5^-) as a primary oxidant cannot be conclusively ruled out at this time.[14] An important difference was found in these in situ oxidations depending upon the use of a homogeneous or a biphasic reaction medium. A biphasic process containing CH_2Cl_2 gave mainly nitroso dimer **4a**, accompanied by smaller amounts of **3a**, **5a**, and a new material identified as oxaziridine **11a** (10% yield). Oxaziridine **11a** was formed as the major product upon submission of imine **9a** to these in situ reaction conditions, although some **4a** and **5a** were also generated. Thus, it is likely that **11a** arises from imine **9a** which is formed from amine **2a** and acetone under the oxidation conditions. Caroate is probably the functioning oxidant for the **9a** → **11a** conversion (vide infra). A preparative experiment in which the crude product from an in situ oxidation of **2a** was treated with Et_3N prior to purification gave oxime **3a** in 58% isolated yield. Although less efficient than the procedure using a solution of **1**, this method avoids the need to prepare **1** and it can be scaled up more readily.

Interestingly, in situ oxidation without the CH_2Cl_2 phase gave more of the nitro compound (Table II), whereas oxaziridine **11a** was not present in the product mixture. Thus, oxidation of **2a** with 16 equiv of oxone gave an 86:14 ratio of **5a**:**4a**. A preparative experiment using 20 equiv of oxone provided nitrocyclohexane (**5a**) in 65% isolated yield. This is clearly the best synthetic method for nitroalkane **5a** of the many examined in this study. In this procedure the intermediates remain in the aqueous oxidation medium rather than being extracted into a protective organic layer as they are in the biphasic reactions.

(14) Kennedy, R. J.; Stock, A. M. *J. Org. Chem.* **1960**, *25*, 1901.

This apparently promotes oxidation all the way to **5a**. Any oxaziridine formed in the homogeneous reaction is probably oxidatively cleaved to acetone and nitrosoalkane **7a**, which then goes on to **5a**. Such a conversion has been documented for peracid oxidations of oxaziridines.[15]



The oxidation of n-butylamine (**2b**) with 6 equiv of **1** in the presence of K_2CO_3 gave a mixture of stereoisomeric oximes **3b** and nitroso dimer **4b**. Treatment of the crude product from a similar reaction with Et_3N generated a 56% yield of oxime **3b**. Interestingly, a third component was isolated in up to 20% yield when K_2CO_3 was omitted from the reaction mixture. This new compound was assigned the nitrone structure **12b** on the basis of characteristic spectroscopic data which include ^1H NMR methyl singlets at δ 2.16 and 2.10 and a methylene triplet (J = 7.5 Hz) at 3.83; ^{13}C NMR signals for the nitrogen bound carbons at δ 143.9 and 58.8 and a band at 1607 cm^{-1} in the IR.[16] The formation of **12b** is believed to involve oxidation of transient imine **9b**. The oxidation of imines with **1** has been shown to yield nitrones.[17] In accord with this, nitrone **12b** was generated in modest amounts upon exposure of authentic imine **9b** to a solution of **1**.

A biphasic oxidation of **2b** by 4.5 equiv of oxone in aqueous acetone–CH_2Cl_2 gave approximately equivalent amounts of oxime **3b**, dimer **4b**, and oxaziridine **11b**, along with a small amount of ntiro compound **5b**. A similar reaction without CH_2Cl_2 gave a mixture of **3b**, **4b**, and **5b** but no **11b**. In this case, increasing the amount of oxone substantially did not improve the yield of nitroalkane. It seems likely that oxaziridine is produced from imine **9b** by a process initiated by the nucleophilic addition of caroate to the imine function. This is analogous to the addition–elimination mechanism proposed for the peracid conversion of imines to oxaziridines[17] and explains the dichotomy in the oxidations of imine **9b** with solutions of **1** (direct oxygen transfer to nitrogen giving nitrone **12b**) relative to the in situ reactions (formation of oxaziridine **11b**). Preparative conversion to oxime **3b** was effected by Et_3N isomerization of the crude oxidation product from an in situ oxidation in 46% yield.

Oxidations of benzylamine (**2c**) with solutions of **1** in the usual manner gave oxime **3c** as a 9:1 mixture of *E* and *Z* isomers as the only important product regardless of the reaction conditions (Table I). Neither nitroso nor nitro compounds were found in these oxidations. A biphasic in situ oxidation of **2c** with 6 equiv of oxone also generated oxime **3c** in modest yield (55%). The crude product from this reaction contained a second unisolated component tentatively assigned as oxaziridine **11c** that decomposed upon chromatography. In order to facilitate the isolation of **3c**, the crude product was heated with Et_3N in hexane

(15) Emmons, W. D. *J. Org. Chem.* **1957**, *79*, 6522.

(16) For a review of nitrone chemistry, see: Breuer, E.; Aurech, H. G.; Nielsen, A. *Nitrones, Nitronates and Nitroxides*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989.

(17) Boyd, D. R.; Coulter, P. B.; McGuckin, R.; Sharma, N. D.; Jennings, W. B.; Wilson, V. E. *J. Chem. Soc., Perkin Trans. 1* **1990**, 531.

prior to purification. This transformed **11c** to benzaldehyde (31% yield) which was easily separated from **3c**. This conversion of **11c** is fully consistent with known chemistry of oxaziridines.[18] The homogeneous in situ oxidation process gave oxime **3c** in comparable yield but in higher purity. The phenyl substituent in this system clearly facilitates the formation of **3c** from the intermediate nitrosoalkane so that most of the starting amine is channeled to this product.

A brief study of the long-chain *n*-decylamine (**2d**) supplemented these results. Thus, oxidations with solutions of **1** gave oxime **3d** (a mixture of *E* and *Z* isomers) and nitroso dimer **4d**, with the former predominating in this case. In experiments without added K_2CO_3 a small amount of a material tentatively identified as nitrone **12d** was also observed in the crude product by NMR. Oxidation in situ with 4.5 equiv of oxone in the absence of an organic phase gave only dimer **4d** (64%) and nitroalkane **5d** (9%) as significant products. However, biphasic oxidation once again led to oxaziridine formation. Thus, a mixture of **11d** (37%), **3d**, and **4d** was isolated from a reaction containing CH_2Cl_2. Preparative conversion of **2d** to aldoxime **3d** in 59% yield was effected by sequential oxidation and Et_3N treatment using the first in situ method.

Finally, allenic amine **2e** was found to undergo oxidation of the amino group without serious compromise of the reactive allene moiety. Thus, oxidation of **2e** with 6 equiv of **1** in the presence of K_2CO_3 gave a 45% yield of a 6:1 mixture of oxime **3e** (1:1 *E*:*Z* ratio) and dimer **4e**. A similar reaction which was heated with Et_3N prior to purification gave **3e** in 47% yield. An experiment without K_2CO_3 produced nitrone **12e** (28%) in addition to **3e** and **4e**. Although the yields were modest in this case, where competing oxidation of the allene unit is possible,[19] a synthetically useful conversion to the oxime was possible.

Conclusions. The oxidation of aliphatic primary amines by dimethyldioxirane is more complicated than previously indicated; oximes, nitroso dimers, nitroalkanes, nitrones, and oxaziridines can all be important products under certain conditions with specific amines. Oximes can be obtained preparatively by a two-step protocol involving oxidation by **1** (or more conveniently in situ by oxone), followed by Et_3N-promoted conversion of the product mixtures to oximes. The nitroso dimers can be isolated in reasonable yields from the initial reaction mixture in most cases. The use of a large excess of oxone in aqueous acetone was employed for the preparative oxidation of **1a** to **5a**; unfortunately, this procedure was not successful for amines with a primary alkyl substituent. Furthermore, we were unable to isolate simple hydroxylamine derivatives in this work and believe that the presence of additional polar functionality in the reported examples[8] of this transformation may be required for efficient conversions to this intermediate oxidation state. Finally, the oxidative condensations of amines with acetone, which gave either nitrones or oxaziridines depending on the reaction conditions, provide direct routes to these novel materials, albeit in relatively low yields.

Experimental Section

General. Melting points are not corrected. ^1H NMR spectra were taken on $CDCl_3$ solutions at 500 MHz; ^{13}C NMR spectra were recorded at 125 MHz. Mass spectra were obtained using chemical (CI) or electron impact (EI) ionization. Exact mass measurements are reported for the M + 1 or M peak. Preparative thin-layer chromatography (TLC) was performed on Kieselgel 60F 254 silica gel on 10- × 20-cm plates of 0.25-mm thickness. Flash chromatography was done with Merck silica gel 60 (250–400 mesh).

Solvents and Reagents. Commercially available reagents were used without purification except for the amines which were distilled from potassium hydroxide.

Dimethyldioxirane Solutions. The simplified version of the procedure for the preparation of **1** was used.[19] The solutions of **1** thus obtained were dried over K_2CO_3, filtered, and stored over 3A molecular sieves at −15 °C before use. Solutions of **1** were titrated by a procedure similar to that described by Baumstark;[20] concentrations were usually in the range of 0.09–0.12 M.

5-Methyl-3,4-hexadien-1-ylamine (2e).[21] To a stirred solution of 8.2 g (31 mmol) of 5-methyl-3,4-hexadien-1-yl *p*-toluenesulfonate[22] in 100 mL of DMF under N_2 was added 6.5 g (100 mmol) of sodium azide. The reaction mixture was stirred overnight and poured into 200 mL of ether. The ether layer was washed three times with brine, dried ($MgSO_4$), and concentrated to give 4.4 g of crude azide: ^1H NMR δ 4.95 (m, 1), 3.30 (t, 2, J = 6 Hz), 2.22 (q, 2, J = 6 Hz), 1.70 (d, 6, J = 3 Hz); ^{13}C NMR δ 202.4, 96.4, 65.0, 50.8, 28.7, 20.5; IR 2099, 1971 cm^{-1}. To a stirred solution of 2.3 g (60 mmol) of $LiAlH_4$ in 200 mL of anhydrous ether under N_2 at 0 °C was added the crude azide in 100 mL of ether. The reaction mixture was stirred overnight at room temperature, cooled to 0 °C, and 11 mL of H_2O and then 2 mL of 10% NaOH were added. After 0.5 h the reaction mixture was dried (K_2CO_3), filtered, and concentrated to give 2.44 g (71%) of **2e** of good purity which was stored at −15 °C under N_2: ^1H NMR δ 4.84 (m, 1), 2.68 (t, 2, J = 7 Hz), 2.01 (q, 2, J = 7 Hz), 1.63 (d, 6, J = 3 Hz), 1.31 (s, 2); ^{13}C NMR δ 202.4, 95.1, 86.1, 41.6, 33.5, 20.7; IR 3368, 3297, 1968, 1580 cm^{-1}; MS (CI) m/z (rel intensity) 112 (22), 111 (100), 96 (64), 84 (48), 82 (30), 79 (44), 67 (52); exact mass 112.115, calculated for $C_7H_{14}N$ 112.1126.

General Procedure for the Oxidation of Amines with Solutions of 1. To a solution of the amine in acetone was added a cold solution of **1**, usually in portions, until the starting material was consumed as determined by GC or TLC. A large excess of oxidant was generally used. Solid $NaHCO_3$ or K_2CO_3 was sometimes added to the reaction mixture as a buffering agent. The reaction mixture was concentrated, dissolved in CH_2Cl_2, dried over K_2CO_3, and concentrated again. After analysis by NMR or GC, the crude product was usually purified by preparative TLC or flash chromatography. Additional details are indicated below for specific substrates.

General Procedure for in Situ Oxidations. Two methods were used. Method A involved stirring a mixture of the amines, 10 g of $NaHCO_3$, and an appropriate amount of oxone in a biphasic solvent mixture consisting of 30 mL each of water, acetone, and CH_2Cl_2. After the oxidant was consumed, the reaction mixture was extracted with ether and the organic layer was washed with brine, dried (K_2CO_3), and concentrated. After analysis of the crude product by NMR, purification by flash chromatography was normally used to separate the components. Method B was performed in a similar manner, except that the CH_2Cl_2 was omitted from the reaction mixture. Further details are indicated below under the specific starting amine.

Oxidation of Cyclohexylamine (2a). A. To 50 mg (0.5 mmol) of **2a** in a 1:3 acetone–dichloromethane solution (40 mL) was added 30 mL (7 equiv) of **1**. Workup and preparative TLC using 1:1 ether–pentane gave 11 mg (20%) of **3a**[9d,f,23] and 27 mg (48%) of **4a** as a white solid:[9a] mp 111–113 °C (lit. mp 118–119 °C).

B. The reaction of 93 mg of **2a** with 42 mL (5 equiv) of **1** and 5 g of $NaHCO_3$ gave, after preparative TLC using 1:1 ether–pentane, 22 mg (21%) of **3a** and 49 mg (46%) of **4a**.

C. Reaction of 78 mg of **2a** with 39 mL (5 equiv) of **1** and 4 g of K_2CO_3 gave 23 mg (25%) of **3a** and 28 mg (33%) of **4a**.

(18) Haddadin, M. J. In *Small-Ring Heterocycles*; Hassner, A., Ed.; Wiley Interscience: New York, 1985; Part 3, p 322.
(19) Crandall, J. K.; Batal, D. J.; Sebesta, D. P.; Lin, F. *J. Org. Chem.* **1991**, *56*, 1153.
(20) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1988**, *53*, 3437.
(21) Bose, A. K.; Kistner, J. K.; Farber, L. *J. Org. Chem.* **1962**, *27*, 2925.
(22) Crandall, J. K.; Tindell, G. L.; Manmade, A. *Tetrahedron Lett.* **1982**, *23*, 3769.
(23) Hawkes, G. E.; Herwig, K.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 1017.

D. Reaction of 80 mg of **2a** with 27 mL (3.5 equiv) of **1** gave 36 mg (40%) of **3a** and 21 mg (21%) of **4a**.

E. To 41 mg of **2a** in 8 mL of acetone was added 78 mL (10 equiv) of **1** in portions. After 10 min, workup and preparative TLC using 50% ether–pentane gave 21 mg (24%) of **3a** and 34 mg (39%) of **4a**. ^{1}H NMR analysis showed only traces of **5a**.

F. To 74 mL (10 equiv) of **1** was added dropwise 73 mg of **2a** in 10 mL of acetone. After 15 min, 75 mg of a 10:50:40 mixture of **3a**, **4a**, and **5a** was obtained.

G. To 35 mg of **2a** in 2 mL of acetone was added 25 mL (7 equiv) of **1** in one portion. After 15 min, 35 mg of a 60:40 mixture **3a** and **5a** was obtained. An experiment with the exclusion of light using 35 mg of **2a** in 5 mL of acetone and 25 mL (7 equiv) of **1** afforded 39 mg of a 70:30 mixture of **4a** and **5a**.

H. To 54 mg of **2a** at −78 °C was added 6.5 mL (1.2 equiv) of **1**. After 15 min, workup gave 55 mg of a yellow oil. ^{1}H NMR showed **4a**, **9a**,[24] **3a**, and **1a** in a ratio of 16:39:39:6. ^{1}H NMR displayed traces of **5a** but no **6a**. After the oil was allowed to stand for 1 day, re-analysis displayed **3a**, **2a**, **1a** and acetone, but no **9a**.

I. To 78 mg of **10** in 5 mL of acetone was added 38 mL (6.5 equiv) of **1**. After 1 h, 60 mg of a 90:10 mixture of **3a**:**5a** was obtained.

J. To 20 mL (10 equiv) of **1** was added dropwise 20 mL of an acetone solution of 26 mg of **10** and 0.3 mL of water. After 30 min, 25 mg of a 26:53:21 mixture of **4a**:**5a**:**10** was obtained. A similar experiment run overnight gave essentially the same product ratio.

K. In situ oxidation by method A of 560 mg of **2a** with 8.6 g (4.5 equiv) of oxone gave, after flash chromatography using 1:1 ether–pentane, 75 mg (10%) of **5a**, 80 mg (10%) of **11a**, 274 mg (43%) of **4a**, and 60 mg (10%) of **3a**. 2-Cyclohexyl-3,3-dimethyloxaziridine (**11a**) was obtained as a yellow liquid:[24] ^{1}H NMR δ 2.26 (tt, 1, J = 11, 4 Hz), 2.00–1.10 (m, 10), 1.52 (s, 3), 1.40 (s, 3); ^{13}C NMR (DEPT) δ 81.1 q, 61.5 t, 31.8 s, 29.1 s, 26.3 p, 25.6 s, 24.4 s, 24.1 s, 17.1 p; MS (EI) m/z (rel intensity) 156 (17), 138 (55), 124 (10), 98 (65), 83 (44), 82 (23), 74 (100). A similar experiment using 8 equiv of oxone gave a 12:60:14:14 mixture of **3a**:**4a**:**5a**:**11a**; one using 16 equiv of oxone gave a 12:50:18:20 mixture of the same products.

L. In situ oxidation by method B of 585 mg of **2a** with 31.9 g (16 equiv) of oxone gave 648 mg (84%) of a 14:86 mixture of **3a** and **5a**. A similar experiment with 1.17 g of **2a** and 79 g (20 equiv) of oxone gave, after flash chromatography using 10% ether–pentane, 140 mg (11%) of **4a** and 990 mg (65%) of **5a**[25] as a yellow liquid: ^{1}H NMR δ 4.35 (tt, 1, J = 10, 4 Hz), 2.25–2.15 (m, 2), 1.90–1.75 (m), 1.70–1.60 (m), 1.40–1.10 (m); ^{13}C NMR δ 84.5, 30.8, 24.7, 23.9. With 8 equiv of oxone a 2:26:72 mixture of **3a**:**4a**:**5a** was observed.

Oxidation of *n*-Butylamine (2b). A. To a solution of 37 mg of **2b** in 2 mL of acetone and 3 g of K_2CO_3 was added 30 mL (6 equiv) of **1**. Preparative TLC using 35% ether–pentane gave 32 mg (74%) of a 22:78 mixture of **3b**[9f,23] (1:1 E:Z ratio) and **4b**: ^{1}H NMR δ 4.26 (t, 4, J = 6.5 Hz), 1.85 (quintet, 4, J = 7.5 Hz), 1.39 (sextet, 4, J = 7.5 Hz), 0.95 (t, 6, J = 7.5 Hz); ^{13}C NMR δ 58.7, 26.8, 19.8, 13.4; IR 1200 cm^{-1}; MS (CI) m/z (rel intensity) 175 (100), 174 (70), 157 (9), 144 (13), 119 (24); exact mass 175.143, calculated for $C_8H_{19}N_2O_2$ 175.1446.

B. To a solution of 59 mg of **2b** in 2 mL of acetone was added 44.5 mL (5 equiv) of **1**. Preparative TLC using 35% ether–pentane gave 32 mg (54%) of a 37:63 mixture of **4b**:**3b** (1:1 E:Z) and 20 mg (20%) of *N*-isopropylidenebutylamine *N*-oxide (**12b**) as a yellow oil: ^{1}H NMR δ 3.83 (t, 2, J = 7.5 Hz), 2.16 (s, 3), 2.10 (s, 3), 1.79 (quintet, 2, J = 7.5 Hz), 1.33 (sextet, 2, J = 7.5 Hz), 0.93 (t, 3, J = 7.5 Hz); ^{13}C NMR δ 143.9, 58.8, 29.4, 20.4, 20.0, 19.9, 13.8; IR 1607, 1374, 1233, 1171 cm^{-1}; MS (CI) m/z (rel intensity) 130 (23), 129 (20), 114 (100), 100 (14); exact mass 130.123, calculated for $C_7H_{16}NO$ 130.1231.

C. A similar reaction with 37 mg of **2b** in 2 mL of acetone and 35 mL (6 equiv) of **1** in the presence of 3 g of $NaHCO_3$ gave 10 mg (15%) of **12b** and 26 mg (60%) of a 60:40 mixture of **4b** and **3b**.

D. In situ oxidation by method A of 455 mg of **2b** with 9.5 g (4.5 equiv) of oxone gave after flash chromatography using 10% ether–pentane 1-butyl-3,3-dimethyloxaziridine (**11b**) as a volatile yellow liquid (27% of crude product):[26] ^{1}H NMR δ 2.80 (ddd, 1, J = 14.5, 8.0, 6.5 Hz), 2.65 (ddd, 1, J = 14.5, 8.0, 6.5 Hz), 1.6–1.7 (m, 2), 1.52 (s, 3), 1.42 (s, 3), 0.93 (t, 3, J = 7.5 Hz); ^{13}C NMR δ 80.9, 54.1, 30.5, 25.9, 20.5, 17.1, 13.9; MS (CI) m/z (rel intensity) 129 (2), 114 (74), 100 (5), 98 (84), 70 (100). Continued elution with 1:1 ether–pentane gave 293 mg (54%) of a 55:45 mixture of **4b** and **3b** (1:1 E:Z ratio).

F. In situ oxidation by method B of 740 mg (10 mmol) of **2b** with 15.4 g (4.5 equiv) of oxone gave 660 mg (80%) of a 50:50 mixture of **4b** and **3b**. About 12% of the crude product was **5b** by ^{1}H NMR analysis.

Oxidation of Benzylamine (2c) A. To a solution of 77 mg of **2c** in 5 mL of acetone with 5 g of $NaHCO_3$ was added 40.5 mL (6 equiv) of **1**. Preparative TLC using 1:1 ether–pentane gave 60 mg (69%) of a 9:1 mixture of E- and Z-**3c**.

B. A similar experiment with 79 mg of **2c**, 5 g of K_2CO_3, and 52 mL (6 equiv) of **1** gave 58 mg (65%) of an 8:1 mixture of E- and Z-**3c**.

C. An experiment with 100 mg of **2c** and 104 mL (6 equiv) of **1** gave 68 mg (60%) of **3c**.

D. In situ oxidation by method A was performed on 680 mg of **2c** with 12 g (6 equiv) of oxone. Analysis of the crude product showed a 38% component tentatively assigned as 1-benzyl-3,3-dimethyloxaziridine[24] (**11c**) by ^{1}H NMR: 3.98 (d, 1, J = 14 Hz), 3.93 (d, 1, J = 14 Hz), 1.66 (s, 3), 1.50 (s, 3). The crude product was refluxed overnight in hexane (250 mL) containing 0.82 mL of Et_3N. Concentration and flash chromatography using 5% ether–pentane gave 209 mg (31%) of benzaldehyde and 341 mg (45%) of E-**3c** as a light yellow solid:[9d,27] mp 28–29 °C (lit. mp 35 °C); ^{1}H NMR δ 9.10 (bs, 1), 8.20 (s, 1), 7.60–7.50 (m, 2), 7.40–7.20 (m, 3); ^{13}C NMR δ 150.4, 131.8, 130.1, 128.8, 127.1; IR 3578, 3314, 3135, 3069, 3019, 2783, 1632, 1601, 1578, 1498, 951, 692 cm^{-1}; MS (CI) m/z (relative intensity) 122 (16), 121 (73), 120 (18), 119 (16), 105 (10), 103 (100), 91 (41), 77 (66). Elution with ether afforded 73 mg (10%) of 90% pure Z-**3b** as a white solid:[28] ^{1}H NMR δ 9.00 (bs, 1), 7.95 (m, 2), 7.50–7.30 (m, 4); ^{13}C NMR δ 147.0, 130.9, 130.4, 130.1, 128.5.

E. In situ oxidation by method B of 540 mg of **2c** with 10 g (6 equiv) of oxone gave, after flash chromatography using 5% ether–pentane, 310 mg (52%) of a 9:1 mixture of E- and Z-**3c**.

Oxidation of *n*-Decylamine (2d). A. To a solution of 40 mg of **2d** in 2 mL of acetone and 4 g of K_2CO_3 was added 21.5 mL (6 equiv) of **1**. Preparative TLC using 40% ether–pentane gave 40 mg (91%) of a 20:80 mixture of **4d** and **3d**[29] (1:1.3 E:Z ratio).

B. An experiment with 49 mg of **2d** and 20.5 mL (6 equiv) of **1** in the presence of 4 g of $NaHCO_3$ gave 31 mg (56%) of a 23:77 mixture of **4d** and **3d** (1:1.6 E:Z ratio). The crude product contains 17% of a third unisolated compound tentatively assigned as *N*-isopropylidenedecylamine *N*-oxide (**12d**) [^{1}H NMR δ 3.85 (t, 2, J = 7.5 Hz), 2.16 (s, 3), 2.11 (s, 3)] and 3% of **5d**.

C. A similar experiment with 40 mg of **2d** and 15 mL (6 equiv) of **1** gave 31 mg (69%) of a 26:74 mixture of **4d** and **3d** (1.3:1 E:Z ratio). The crude product showed 8% of **5d** and ca. 3% of **12d**.

D. In situ oxidation by method A of 480 mg of **2d** with 4.5 g (4.5 equiv) of oxone after flash chromatography using 10% ether–pentane gave 235 mg (37%) of **11d** and 260 mg (50%) of a 70:30 mixture of **4d** and **3d** (2.5:1 E:Z ratio). 2-Decyl-3,3-dimethyloxaziridine (**11d**) was obtained as a yellow liquid: ^{1}H NMR δ 2.79 (ddd, 1, J = 14.5, 8.0, 6.5 Hz), 2.64 (ddd, 1, J = 14.5, 8.0, 6.5 Hz), 1.50–1.70 (m, 2), 1.51 (s, 3), 1.41 (s, 3), 1.10–1.50 (m, 14), 0.86 (t, 3, J = 7 Hz); ^{13}C NMR δ 80.9, 54.4, 31.8, 29.51, 29.48, 29.46, 29.3, 28.4, 27.4, 25.9, 22.6, 17.1, 14.05; IR 1378, 1343, 1242, 1125, 824, 721 cm^{-1}; MS (CI) m/z (rel intensity) 214 (3), 198 (29), 196 (27), 126 (12), 112 (12), 87 (12), 85 (17), 84 (22), 83 (10), 74 (14), 73

(24) Black, D. S.; Blackman, N. A. *Aust. J. Chem.* **1975**, *28*, 2547.
(25) Franklin, N. C.; Feltkamp, H. *Tetrahedron* **1966**, 2801.
(26) Schulz, M.; Rieche, A. *Chem. Ber.* **1966**, *99*, 3233.
(27) Vauk, C. P. J.; Hasan, M.; Holloway, C. E. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1214.
(28) Schovenewaldt, E. F.; Kinnel, R. B.; Davis, P. *J. Org. Chem.* **1968**, *33*, 4270. Ooi, N. S.; Wilson, D. A. *J. Chem. Res. Synop.* **1981**, 18.
(29) Geiseler, G.; Lueck, S.; Fruivert, J. *Spectrochim. Acta, Part A* **1975**, *31A*, 789.

(19), 70 (100); exact mass 214.218, calculated for $C_{13}H_{28}NO$ 214.2170.

F. In situ oxidation by method B of 393 mg of **2d** with 4 g (4.5 equiv) of oxone, after flash chromatography using 10% ether–pentane, gave 272 mg (64%) of **4d** as a white solid: mp 64–65 °C; ^{1}H NMR δ 4.24 (t, 4, J = 7 Hz), 1.84 (quintet, 4, J = 7 Hz), 1.2–1.4 (m, 28), 0.86 (t, 6, J = 7 Hz); ^{13}C NMR δ 58.9, 31.8, 29.4, 29.3, 29.2, 29.0, 26.6, 25.0, 22.6, 14.0; IR 1377, 1238, 1190 (s), 750 cm^{-1}; MS (CI) m/z (rel intensity) 172 (8), 86 (11), 85 (48), 71 (51), 57 (100); exact mass 172.170, calculated for $C_{10}H_{22}NO$ (monomer + 1) 172.1701. Also obtained was 43 mg (9%) of 1-nitrodecane (**5d**) as a yellow liquid:[30] ^{1}H NMR δ 4.36 (t, 2, J = 7.5 Hz), 1.99 (quintet, 2, J = 7.5 Hz), 1.1–1.5 (m, 14), 0.86 (t, 3, J = 7.5 Hz); ^{13}C NMR δ 75.6, 31.8, 29.3, 29.21, 29.17, 28.8, 27.4, 26.2, 22.6, 14.0; IR 1553, 1464, 1437, 1381 cm^{-1}; MS (CI) m/z (rel intensity) 188 (7), 97 (27), 85 (32), 83 (64), 71 (42), 69 (79), 57 (65), 55 (100). The crude product contained 13% of **11d**.

Oxidation of 5-Methyl-3,4-hexadienylamine (2e). A. To 55 mg of **2e** and 3 g of K_2CO was added 30 mL (6 equiv) of **1**. Preparative TLC using 40% ether–pentane gave 30 mg (48%) of a 83:17 mixture of **3e** (1:1 E:Z ratio) and **4e**: ^{1}H NMR δ 4.96 (m, 2), 4.31 (t, 4, J = 6 Hz), 2.50 (t, 4, J = 6 Hz), 1.66 (d, 12, J = 3 Hz); ^{13}C NMR δ 202.2, 97.2, 84.3, 58.1, 24.6, 20.5; IR 1190 cm^{-1}.

B. A similar reaction with 55 mg of **2e** in 10 mL of acetone and 32 mL (6 equiv) of **1** in the presence of 5 g of $NaHCO_3$ gave 27 mg (45%) of an 80:20 mixture of **3e** and **4e**.

C. To 63 mg of **2e** in 2 mL of acetone was added 28 mL (5 equiv) of **1**. Preparative TLC using 40% ether–pentane afforded 26 mg (28%) of *N*-isopropylidene-5-methyl-3,4-hexadien-1-ylamine *N*-oxide (**12e**) as a yellow oil and 17 mg (25%) of an 80:20 mixture of **3e** and **4e**. Compound **12e** shows: ^{1}H NMR δ 4.97 (m, 1), 3.88 (t, 2, J = 7 Hz), 2.54 (q, 2, J = 7 Hz), 2.16 (s, 3), 2.10 (s, 3), 1.67 (d, 6, J = 6 Hz); ^{13}C NMR δ 202.2, 144.1, 96.5, 84.8, 58.1, 29.9, 20.6, 20.5, 20.1; IR 1967, 1607, 1447, 1155, 783, 739 cm^{-1}; MS (CI) m/z (rel intensity) 168 (100), 110 (14), 95 (68), 70 (63); exact mass 168.139, calculated for $C_{10}H_{18}NO$ 168.1388.

Oxidation of 6a. To 23 mg of **6a**:[31] ^{1}H NMR δ 4.19 (tt, 1, J = 11, 4 Hz), 1.0–2.1 (m, 10); ^{13}C NMR (acetone) δ 65.3, 30.4, 25.9, 25.5, was added 4.5 mL (2.5 equiv) of **1**. The reaction mixture was stirred for 15 min and worked up to give 24 mg (100%) of a 50:50 mixture of **3a** and **4a**.

Oxidation of 3a. To 41 mg of **3a** in 5 mL of acetone was added 19 mL (5 equiv) of **1**. The reaction mixture was stirred 5 h and processed to give 38 mg (95%) of a 60:40 mixture of **3a** and cyclohexanone.

Oxidation of 4a. To 74 mg of **4a** was added 16 mL (5 equiv) of **1**. The reaction was stirred 6 h and processed to give 74 mg of a 90:10 mixture of **4a**:**5a**.

Oxidation of 9c. To 52 mg of **9c**[32] [^{1}H NMR δ 3.17 (t, 2, J = 7.5 Hz), 1.98 (t, 3, J = 1 Hz), 1.80 (s, 3), 1.58 (quin, 2, J = 7.5 Hz), 1.35 (sex, 2, J = 7.5 Hz), 0.91 (t, 3, J = 7.5 Hz); ^{13}C NMR δ 156.6, 51.2, 32.9, 29.2, 20.7, 18.2, 13.9] in 2 mL of acetone was added 21 mL (4.5 equiv) of **1**. After 15 min, processing gave 42 mg of a 44:30:26 mixture of **3c**, **4c**, and **12c**.

In Situ Oxidation of 9a. To a solution of 10 g of $NaHCO_3$ in 30 mL of water and 30 mL of acetone was added 140 mg of **9a** [^{1}H NMR δ 3.17 (tt, 1, J = 11, 4 Hz), 1.94 (s, 3), 1.80 (s, 3), 1.0–1.8 (m, 10)] in 30 mL of CH_2Cl_2 and 1.5 g (4.5 equiv) of oxone. Workup gave 96 mg of a 73:22:5 mixture of **11a**, **5a**, and **4a**.

Cyclohexanone Oxime (3a). To a solution of 72 mg of **2a** in 10 mL of acetone and 30 mL of CH_2Cl_2 was added 50 mL (7 equiv) of **1** in portions. The reaction mixture was concentrated, dissolved in CH_2Cl_2, dried over K_2CO_3, and reconcentrated to give a 30:70 mixture of **3a** and **4a**. This product was refluxed overnight in 30 mL of hexane containing 56 μL of Et_3N. Concentration and flash chromatography using 1:1 ether–pentane gave 57 mg (70%) of **3a** as a white solid:[9d,f] mp 88–89.5 °C (lit. mp 89–90 °C); ^{1}H NMR δ 7.70 (bs, 1), 2.50 (t, 2, J = 6.5 Hz), 2.20 (t, 2, J = 6.5 Hz), 1.40–1.70 (m, 6).

Oxidation of 554 mg of **2a** with 15.1 g (8 equiv) of oxone and 10 g of $NaHCO_3$ in 30 mL of water, 30 mL of acetone, and 30 mL of CH_2Cl_2, followed by heating the crude isolated product to reflux in 220 mL of hexane containing 0.9 mL of Et_3N overnight, gave, after concentration and chromatography, 364 mg (58%) of **3a**.

Butanal Oxime (3b). The product from oxidation of 37 mg of **2b** in 2 mL of acetone with 30 mL (6 equiv) of **1** in the presence of 3 g of K_2CO_3 was heated to reflux for 1 h in 20 mL of hexane containing 60 μL of Et_3N. Concentration and flash chromatography using 40% ether–pentane gave 24 mg (56%) of a 1:1 E:Z mixture of **3b** as a yellow liquid:[9f] The E oxime shows ^{1}H NMR δ 9.0 (bs, 1), 7.41 (t, 1, J = 6 Hz), 2.18 (td, 2, J = 7.5, 6 Hz), 1.51 (sextet, 2, J = 7.5 Hz), 0.96 (t, 3, J = 7.5 Hz). The Z oxime shows ^{1}H NMR δ 9.5 (bs, 1), 6.71 (t, 1, J = 5.5 Hz), 2.36 (td, 2, J = 7.5, 5.5 Hz), 1.51 (sextet, 2, J = 7.5 Hz), 0.96 (t, 3, J = 7.5 Hz).

Oxidation of 607 mg of **2b** with 12.6 g (4.5 equiv) of oxone and 10 g of $NaHCO_3$ in 30 mL each of acetone and water followed by isomerization of crude product as above gave 335 mg (46%) of **3b** as a 1:1 mixture of isomers.

Decanal Oxime (3d). Oxidation of 520 mg of **2d** with 5.1 g (4.5 equiv) of oxone and 10 g of $NaHCO_3$ in 30 mL each of water and acetone followed by treatment with Et_3N in hexane as above gave 335 mg (59%) of a 1:1 E:Z mixture of **3d** as a white solid:[29] IR 3585, 3262, 1667 cm^{-1}; ^{13}C NMR δ 153.1 (Z), 152.4 (E), 31.9 (E). Oxime E displays ^{1}H NMR δ 8.50 (bs, 1), 7.41 (t, 1, J = 6 Hz), 2.19 (td, 2, J = 7.5, 6.0 Hz), 1.47 (quintet, 2, J = 7.5 Hz), 1.20–1.40 (m, 12), 0.88 (t, 3, J = 7.5 Hz). Oxime Z displays ^{1}H NMR δ 9.00 (bs, 1), 6.71 (t, 1, J = 5.5 Hz), 2.38 (td, 2, J = 7.5, 5.5 Hz), 1.47 (quintet, 2, J = 7.5 Hz), 1.20–1.40 (m, 12), 0.88 (t, 3, J = 7.5 Hz).

5-Methyl-3,4-hexadienal Oxime (3e). To 36 mg of **2e** and 3 g of K_2CO_3 was added 18 mL (5.5 equiv) of **1**. The isolated crude product in hexane (20 mL) containing 40 μL of Et_3N was refluxed for 1 h and concentrated. Preparative TLC using 40% ether–pentane yielded 19 mg (47%) of a 1:1 E:Z mixture of **3e**: IR 3378, 1969, 1661, 1364, 1233, 916 cm^{-1}; MS (CI) m/z (rel intensity) 126 (58), 100 (22), 108 (100), 98 (50), 81 (50); exact mass 126.090, calculated for $C_7H_{12}NO$ 126.0918; ^{13}C NMR δ 202.7, 202.5, 150.8 (Z), 150.6 (E), 97.1, 96.7, 83.6, 83.4, 29.7 (E), 24.9 (Z), 20.5, 20.4. The E oxime displays ^{1}H NMR δ 8.5 (bs, 1), 7.40 (t, 1, J = 6 Hz), 5.01 (m, 1), 2.85 (t, 2, J = 6 Hz), 1.68 (d, 6, J = 3 Hz). The Z oxime displays ^{1}H NMR δ 9.0 (bs, 1), 6.80 (t, 1, J = 5 Hz), 4.95 (m, 1), 3.03 (dd, 2, J = 6, 5 Hz), 1.69 (d, 6, J = 3 Hz).

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Supplementary Material Available: NMR spectra of **1e**, **3e**, **4d**, **11d**, **12b**, and **12e** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(30) Ono, N.; Jun, T. X.; Kaji, A. *Synthesis* **1987**, 821.
(31) Feuer, H.; Vincent, B. F.; Bartlett, R. S. *J. Org. Chem.* **1965**, *30*, 2877.
(32) Bonnet, R.; Emerson, T. R. *J. Chem. Soc.* **1965**, 4509.