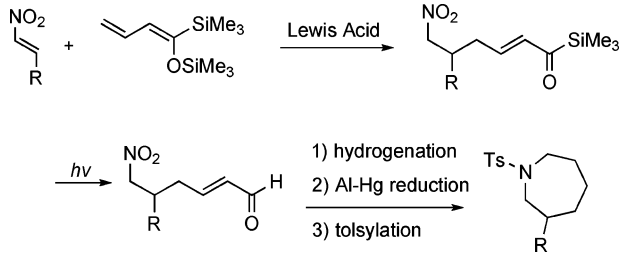
JOC*Note*

Lewis Acid-Promoted Conjugate Addition of Dienol Silyl Ethers to Nitroalkenes: Synthesis of 3-Substituted Azepanes

Scott E. Denmark* and Min Xie

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

Received May 28, 2007



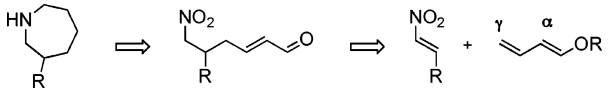
A novel γ-selective conjugate addition of 1-silyl-substituted dienol ethers to nitroalkenes activated by Lewis acids has been developed. The resulting α,β-unsaturated acylsilanes undergo photoinduced protodesilylation to afford the corresponding enals, which can be conveniently transformed into azepanes under appropriate reductive conditions.

Azepanes, 7-membered nitrogen-containing heterocycles are an important structural motif found in a variety of medicinal compounds.[1] These heterocycles have attracted much interest, and their synthesis has been the subject of intensive study. A classic method for the construction of azepanes is the reduction of the corresponding caprolactams which are in turn available from Beckmann rearrangement of cycloalkanone oximes[2] or from the Schmidt reaction of cycloalkanone (which offers complementary regioselectivity).[3] Unfortunately, these two methods, although generally efficient, often generate a mixture of constitutional isomers.[4] Other ring-expansion[5] or rearrangement[6] reactions allow for the formation of 7-membered nitrogen-containing heterocycles from 3-, 4-, 5-, 6-, and 8-membered rings.

Ring-formation processes provide alternative strategies to construct azepanes and their unsaturated analogues. For example, the combination of azadienes with Fischer carbene complexes allows for the asymmetric construction of highly substituted 7-membered heterocycles.[7] Ring-closing metathesis has also been applied in azepane synthesis.[8] In addition, numerous cyclization reactions including nitrogen alkylation, lactamization, or reductive amination processes effect direct construction of 7-membered rings.[6] Recently, an asymmetric synthesis of polysubstituted azepanes was reported by Beak and co-workers that employs an enantioselective conjugate addition of a lithiated allylamine followed by lactamization.[9] Despite these important advances, a general approach for the synthesis of azepanes with a variety of substituents from easily accessible starting materials remains a challenge.

Nitroalkenes are readily available and are versatile building blocks for efficient C−C and C−N bond-formation reactions. Over the past two decades we have extensively investigated and developed the Lewis acid-promoted cycloaddition of enol ethers and nitroalkenes for the construction of monocyclic, fused and spirocyclic nitrogen-containing compounds, notably pyrrolidines and piperidines.[10] Herein we report a novel construction of azepanes that takes advantage of the reactivity of nitroalkenes toward dienol ethers (Scheme 1).

SCHEME 1



For this strategy to succeed, the addition reaction between dienol ethers and nitroalkenes must provide the 1,6-relationship between the nitro and carbonyl functional groups in the adducts, which can be further transformed into azepanes. Because dienol ethers possess two nucleophilic sites, the desired γ-selective nucleophilic addition is not guaranteed. Fortunately, it has been demonstrated that in the presence of Lewis acid activators, dienol ethers undergo Mukaiyama-type vinylogous aldol reactions.[11,12]

To develop an efficient synthesis of azepane precursors, studies commenced with an investigation of the effects of different Lewis acids on the reactivity and selectivity of nitroalkenes toward dienol ethers. Previous studies from this group have already demonstrated that Me_3Al, $Ti(O\textit{i}\text{-}Pr)_2Cl_2$ and $SnCl_4$ are effective Lewis acid promotors for the cycloaddition reactions of nitroalkenes with enol ethers.[10c] Thus, pentadienol ether **2**[13] was prepared as a mixture of (*E*)- and (*Z*)-isomers and was employed in the reaction with nitroalkene **1** (Scheme 2). Although the relatively mild Lewis acid Me_3Al promoted the addition of dienol ether **2** to nitroalkene **1**, the formation of only Diels−Alder product **3** was observed. $SnCl_4$ afforded the same product with higher efficiency. Interestingly, $Ti(O\textit{i}\text{-}Pr)_2Cl_2$ effected the formation of both cyclohexene **3** and α-adduct **4**. Unfortunately, the desired γ-adduct was not obtained in any case.

* To whom correspondence should be addressed. E-mail: denmark@scs.uiuc.edu.

(1) Proctor, G. R.; Redpath, J. *Monocyclic Azepines: The Synthesis and Chemical Properties of the Monocyclic Azepines*; John Wiley & Sons: New York, 1996.

(2) Fernandez, F.; Perez, C. *Heterocycles* **1987**, *26*, 2411−2417.

(3) Georg, G. I.; Guan, X.; Kant, J. *Bioorg. Med. Chem. Lett.* **1991**, *1*, 125−128.

(4) Evans, P. A.; Holmes, A. B. *Tetrahedron* **1991**, *47*, 9131−9166.

(5) Schmitz, E.; Ohme, R.; Schramm, S.; Striegler, H.; Heyne, H.; Rusche. J. *J. Prakt. Chem.* **1977**, *319*, 195−200.

(6) Newkome, G. R. *Comprehensive Heterocyclic Chemistry II, Vol. 9: Seven Membered and Larger Rings and All Fused Derivatives*; Pergamon: NewYork, 1996.

(7) Barluenga, J. *J. Pure Appl. Chem.* **2002**, *74*, 1317−1325.

(8) Li, H.; Blériot, Y.; Chantereau, C.; Mallet, J.; Sollogoub, M.; Zhang, Y.; Rodríguez-García, E.; Vogel, P.; Jiménez-Barbero, J.; Sinaÿ, P. *Org. Biomol. Chem.* **2004**, *2*, 1492−1499.

(9) Lee, S. J.; Beak, P. *J. Am. Chem. Soc.* **2006**, *128*, 2178−2179.

(10) (a) Denmark, S. E.; Thorarensen, A. *Chem. Rev.* **1996**, *96*, 137−165. (b) Denmark, S. E.; Cottell, J. J. Nitronates. In *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry toward Heterocycles and Natural Products*; John Wiley & Sons: New Jersey, 2003; Chapter 2. (c) Denmark, S. E.; Seierstad, M. *J. Org. Chem.* **1999**, *64*, 1610−1619.

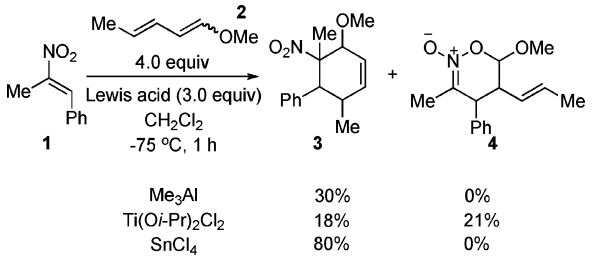
(11) Mukaiyama, T.; Ishida, A. *Chem. Lett.* **1975**, 319−322.

(12) (a) Denmark, S. E.; Heemstra, J. R., Jr.; Beutner, G. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4682−4698. (b) Heemstra, J. R., Jr.; Denmark, S. E. *J. Am. Chem. Soc.* **2006**, *128*, 1038−1039.

(13) Mikami, K.; Motoyama, Y.; Terada, M. *J. Am. Chem. Soc.* **1994**, *116*, 2812−2820.

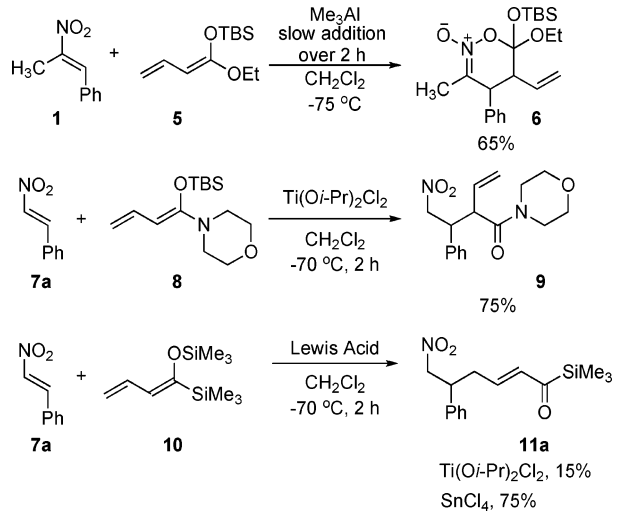
10.1021/jo071126i CCC: $37.00
Published on Web 08/03/2007

SCHEME 2



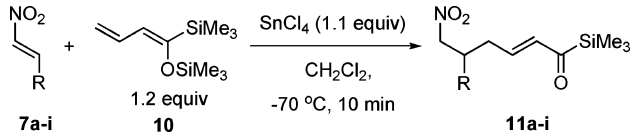
Previous studies in these laboratories have shown that vinyl ketene acetals **5**[12a] and **8**[12b] undergo vinylogous aldol addition reactions and therefore could potentially effect the desired γ-site selectivities in the addition to nitroalkenes. Unfortunately, when the ester-derived dienol ether **5** was combined with nitroalkene **1** in the presence of Me_3Al, only the α-cycloadduct **6** was formed (Scheme 3). Exclusive α-site-selectivity was again observed in the addition of **8** to nitrostyrene **7** to produce **9** in good yield (Scheme 3). To effect the desired γ-site nucleophilic attack while preventing both the α addition and the Diels−Alder pathway, dienol ethers bearing a bulky substituent at C(1) were considered. The acylsilane-derived dienol ether **10** bearing a silyl substituent at C(1) represents this structural characteristic and can be conveniently synthesized from allyltrimethylsilane.[14] Although addition reactions of this 1,1-disubstituted dienol ether find no precedent, we decided to test its behavior in reactions with nitroalkenes. Gratifyingly, **10** underwent addition to 2-nitrostyrene in the presence of $TiCl_2(Oi\text{-}Pr)_2$ with exclusive γ-selectivity, to afford the nitroacylsilane product **11a**. Ultimately, $SnCl_4$ was found to be an effective promotor for generating the conjugate adduct **11a** in good yield (Scheme 3).

SCHEME 3



Optimized conditions for the $SnCl_4$-promoted addition of dienol ether **10** were applied for a variety of nitroalkenes (Table 1). The shortest reaction times and most consistent yields could be achieved by the addition of a solution of $SnCl_4$ to the precooled solution of reactants over 40 s. Both electron-neutral and electron-rich nitroalkenes (entries 1−5) were consumed in 10 min at −70 °C and afforded the desired products in good yields. Yields for electron-poor nitroalkenes (entries 6−9) decreased under the standard conditions, and unreacted nitroalkenes were recovered. This incomplete conversion was likely due to the nonproductive consumption of dienol ether **10**. A control experiment established that, when **10** was combined with $SnCl_4$ under the same conditions, the dienol ether decomposed completely within minutes, at a rate comparable to that of the productive addition to less reactive nitroalkenes. It was also observed that an undesired product arose from the addition of **10** to the acylsilane product.[15] This side reaction, unfortunately, thwarts the use of a large excess of dienol ether.

TABLE 1. Lewis Acid Promoted Conjugate Addition of 10 to Nitroalkenes

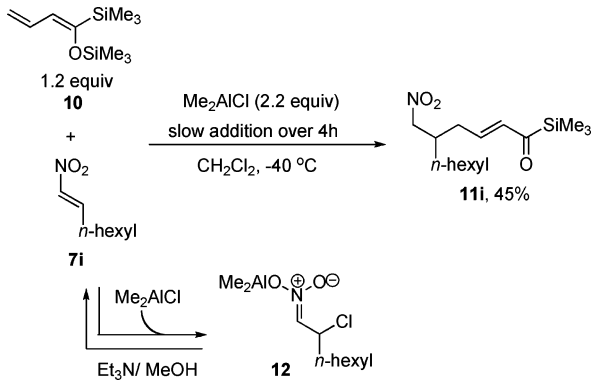


entry	R	product	yield,[a] %
1	C_6H_5	**11a**	75
2	1-naphthyl	**11b**	76
3	2-furyl	**11c**	70
4	2-$MeOC_6H_4$	**11d**	92
5	4-$MeOC_6H_4$	**11e**	90
6	2-ClC_6H_4	**11f**	70
7	4-ClC_6H_4	**11g**	64
8	3-BrC_6H_4	**11h**	55
9	*n*-hexyl	**11i**	15

[a] Yield of analytically pure materials.

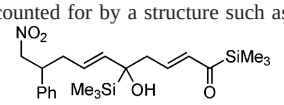
During a survey of Lewis acids, Me_2AlCl was found to be the only suitable reagent to activate aliphatic nitroalkene **7i** (Scheme 4). Unfortunately, under a variety of conditions, the nitroalkene was never consumed. ^1H NMR and ^{13}C NMR analysis of the reaction mixture confirmed that Me_2AlCl reacted with nitroalkene **7i** to afford the corresponding chloride adduct **12**,[16] which was not susceptible toward further nucleophilic attack by the dienol ether **10**. Slow addition of a CH_2Cl_2 solution of Me_2AlCl to the mixture of **7i** and **10** at −40 °C over 4 h, however, afforded **11i** in 45% yield. After quenching the reaction with a methanolic solution of Et_3N followed by aqueous workup, unreacted **7i** and **10** were recovered. Thus, a novel,

SCHEME 4



(14) Ryu, I.; Yamamoto, H.; Sonoda, N.; Murai, S. *Organometallics* **1996**, *15*, 5459−5461.

(15) A side product was isolated from the reaction of **7a** and **10**, which was not stable after isolation and therefore was not fully characterized. It could possibly be accounted for by a structure such as

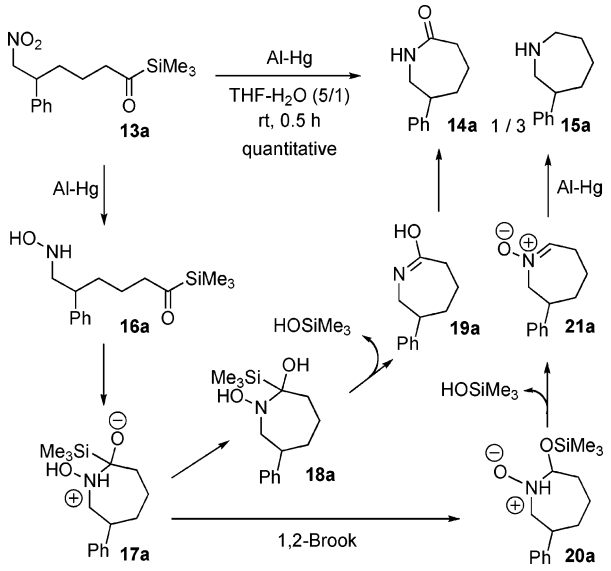


which was suggested by ^1H NMR analysis.

Lewis acid-promoted vinylogous conjugate addition to nitroalkenes affords nitroacylsilanes which are potential precursors to azepanes.

The elaboration of nitroacysilanes into azepanes was expected to be straightforward. Acylsilanes are aldehyde equivalents and are highly susceptible toward nucleophilic attack.[17] To develop an effective process to convert nitroacylsilanes into azepanes, **11a** was chosen as the test substrate. The trans double bond in **11a** was easily saturated through catalytic hydrogenation (1 atm) with Pd/C (10 wt %) in quantitative yield. Among a number of methods investigated for the reduction of nitro group and the concomitant reductive amination, Al−Hg was found to effect the clean conversion of **13a** into a cyclized product (Scheme 5). However, spectroscopic data indicated that a mixture of lactam **14a** and azepane **15a** was obtained. Unfortunately, variation of solvent, pH, or temperature exerted little effect upon the product distribution.

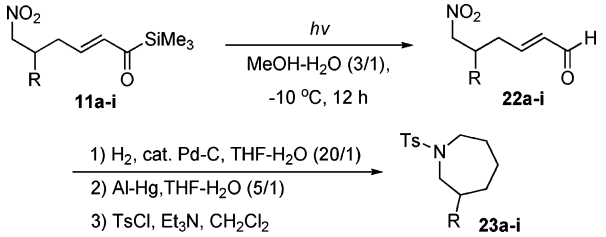
SCHEME 5



A plausible mechanism for the formation of the two products is illustrated in Scheme 5. Reduction of the nitro group affords the hydroxylamine **16a**, which undergoes intramolecular nucleophilic attack onto the acylsilane moiety to afford a zwitterion intermediate **17a** and then eliminates Me_3SiOH (Peterson elimination[18]) and tautomerizes to lactam **14a**. Alternatively, intermediate **17** may undergo a [1,2]-silyl shift (Brook rearrangement[19]) followed by extrusion of Me_3SiOH to afford nitrone **21a** that can be further reduced to azepane **15a**.[20]

To eliminate some of these mechanistic pathways in the tandem reduction/reductive amination sequence, the acylsilane was transformed into an aldehyde. This conversion is easily accomplished by a photoinduced protiodesilylation[21] in a protic solvent to afford the corresponding enals in generally good yields (Table 2). From this success, a streamlined Pd−C-catalyzed hydrogenation followed by Al−Hg reduction process conveniently converted the nitroaldehydes to 3-susbtituted azepanes. The tosyl-protected derivatives were prepared to facilitate isolation and purification.

TABLE 2. Elaboration of α,β-Unsaturated Acylsilanes into *N*-Tosylazepanes



entry	R	enal, yield, [a] %	*N*-tosylazepane, yield, [b] %
1	C_6H_5	**22a**, 78	**23a**, 82
2	1-naphthyl	**22b**, 72	**23b**, 85
3	2-furyl	**22c**, 60	**23c**, 72
4	2-$MeOC_6H_4$	**22d**, 74	**23d**, 92
5	4-$MeOC_6H_4$	**22e**, 75	**23e**, 89
6	2-ClC_6H_4	**22f**, 72	**23f**, 76
7	4-ClC_6H_4	**22g**, 76	**23g**, 70
8	3-BrC_6H_4	**22h**, 70	**23h**, 55
9	*n*-hexyl	**22i**, 75	**23i**, 72

[a] Yield of chromatographically homogeneous products. [b] Yield of analytically pure products.

In summary, a novel, vinylogous conjugate addition of an acylsilane-derived dienol ether to aryl and alkyl substituted nitroalkenes was developed. The nitroacylsilane products were obtained in good to moderate yields. Nitroacylsilanes could be easily converted into the corresponding enals, which were efficiently elaborated into *N*-tosylazepanes in good yield through a streamlined three-step process involving catalytic hydrogenation, reductive amination, and tosylation.

Experimental Section

General Experimental Procedures. See the Supporting Information.

Representative Procedure for $SnCl_4$-Promoted Conjugate Addition of Acylsilane-Derived Dienol Ether (10) to Nitrostyrene (7a). Preparation of Acylsilane 11a. To a cold (−70 °C, internal temperature) solution of nitrostyrene **7a** (175 mg, 1.17 mmol, 1.0 equiv) and dienol ether **10** (515 mg, 1.40 mmol, 1.2 equiv) in dry CH_2Cl_2 (4.0 mL) in a 50-mL, round-bottomed, two-necked flask under nitrogen was added a CH_2Cl_2 solution of $SnCl_4$ (0.50 M, 2.58 mL, 1.29 mmol, 1.1 equiv) dropwise via syringe through a septum over 40 s. The resulting yellow solution was allowed to stir at −70 °C for 10 min. With vigorous stirring, a MeOH solution of Et_3N (1.0 M, 5.7 mL, 5.7 mmol, 4.9 equiv) was rapidly added to the reaction mixture, followed by H_2O (1 mL). The mixture was warmed to ambient temperature and passed through a silica gel plug (3 cm × 2 cm) and then was eluted with CH_2Cl_2 (40 mL). The organic eluent was dried (Na_2SO_4) and concentrated in vacuo. In a dark environment, the organic residue was purified by column chromatography (SiO_2, 30 mm × 20 cm, hexane/EtOAc, 10/1, 8/1, 3/1) to afford 248 mg (73%) of **11a** as a heavy, yellow oil. Data for **11a**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.38−7.29 (m, 3 H,

(16) For spectroscopic data for the chloride adduct, see Supporting Information.

(17) (a) Patrocínio, A. F.; Mora, P. J. S. *J. Braz. Chem. Soc.* **2001**, *12*, 7−31. (b) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147−195. (c) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647−660.

(18) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780−784.

(19) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77−84.

(20) The formation of a lactam (amide) from an acylsilane and a hydroxylamine appears to be unprecedented. However, the analogy to the recently reported peptide ligation of hydroxylamines with α-keto acids is noteworthy. Bode, J. W.; Fox. R. M.; Baucom, K. D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1248−1252.

(21) Brook, A. G.; Duff, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 454−455.

H-phenyl), 7.21−7.18 (m, 2 H, H-phenyl), 6.43 (dt, J = 16.1, 7.1, 1 H, HC(3)) 6.30 (dt, J = 16.1, 1.2, 1 H, HC(2)), 4.61 (d, J = 7.5, 2 H, HC(6)), 3.66, (m, 1 H, HC(5)), 2.66, (m, 2 H, HC(4)), 0.12 (s, 9 H, $(H_3C)_3Si$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 236.5 (C(1)), 142.7 (C(3)), 138.3 (C(2)), 137.9 (C(7)), 129.2 (C(9)), 128.4 (C(10)), 127.4 (C(8)), 79.9 (C(6)), 43.5 (C(5)), 36.2 (C(4)), −2.2 (C(11)); IR (neat): cm^{-1} 3065 (w), 3032 (m), 2959 (m), 2917 (m), 2896 (m), 2361 (w), 2342 (w), 1953 (w), 1876 (w), 1809 (w), 1639 (m), 1590 (s), 1553 (s), 1496 (m), 1455 (m), 1434 (m), 1379 (s), 1259 (s), 1190 (m), 1153 (m), 1089 (w), 980 (m), 846 (s), 762 (m), 701 (m); MS (FI): 291.2 (M^+, 100), 292.2 (24); TLC R_f 0.28 (hexane/EtOAc, 3/1) [silica gel, UV, I_2, CAM]; Anal. Calcd for $C_{15}H_{21}NO_3Si$: C, 61.40; H, 7.90; N, 4.77. Found: C, 61.21; H, 7.87; N, 4.91.

Representative Procedure for Photoinduced Protiodesilylation of α,β-Unsaturated Acylsilane 11a. Preparation of Enal 22a. α,β-Unsaturated acylsilane **11a** (473 mg, 1.62 mmol) was dissolved in MeOH (60 mL) in a 250-mL, round-bottomed flask, and water (20 mL) was added with stirring. The flask was sealed with a septum and was cooled in a cold bath of 2-propanol to maintain an internal temperature at −10 °C by an immersion cooler. The solution was irradiated with light generated from a 250-W bulb 10 cm away from the top of the solution. After irradiation for 12 h, the yellow color of the solution faded. The solution was then concentrated under vacuo to 30 mL and was then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and were then passed through a silica gel plug (3 cm × 3 cm), eluting with CH_2Cl_2 (60 mL). The organic eluent was concentrated, and the residue was purified by column chromatography (SiO_2, 30 mm × 20 cm, hexane/EtOAc, 10/1, 8/1, 6/1, 4/1, 3/1) to afford 267 mg (75%) of **22a** as a colorless, heavy oil. Data for **22a**: ^1H NMR (500 MHz, $CDCl_3$): δ 9.40 (d, J = 7.8, 1H, HC(1)), 7.38−7.29 (m, 3 H, H-phenyl), 7.22−7.18 (m, 2 H, H-phenyl), 6.60 (dt, J = 15.6, 7.1, 1 H, HC(3)) 6.08 (ddq, J = 15.6, 7,8, 1.4, 1 H, HC(2)), 4.61 (t, J = 7.9, 2 H, HC(6)), 3.70, (m, 1 H, HC(5)), 2.77 (m, 2H, HC(4)); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2 (C(1)), 152.5 (C(3)), 137.5 (C(2)), 135.2 (C(7)), 129.3 (C(9)), 128.3 (C(8)), 127.3 (C(10)), 79.9 (C(6)), 43.1 (C(5)), 35.9 (C(4)); IR (neat): cm^{-1} 3358 (w), 3064 (m), 3031 (m), 3007 (m), 2920 (m), 2747 (m), 1858 (w), 1884 (w), 1812 (w), 1691 (vs), 1639 (m), 1604 (m), 1552 (vs), 1495 (m), 1455 (m), 1434 (s), 1380 (s), 1340 (w), 1314 (w), 1203 (w), 1177 (m), 1132 (s), 1087 (m), 1012 (m), 978 (s), 950 (w), 917 (w), 882 (w), 847 (w), 764 (s), 736 (m), 702 (s), 651 (w); TLC R_f 0.14 (hexane/EtOAc, 3/1) [silica gel, UV, I_2, CAM].

Representative Procedure for the Synthesis of *N*-Tosyl Azepane, 23a. Enal **22a** (226 mg, 1.03 mmol) was dissolved in 21 mL of THF−H_2O (20/1) in a 50-mL, round-bottomed flask equipped with a magnetic stir bar. Pd−C (10 wt %, 45 mg) was added. The flask was hooked up to a hydrogenation manifold and the solution stirred vigorously at ambient temperature under an atmosphere of H_2 for 1 h. The reaction mixture was filtered through a silica gel plug (10 mm × 2 cm) with a short pad of Celite on top, eluting with THF (30 mL). H_2O (7 mL) was added to the eluate. The resulting homogeneous solution was transferred to a 100-mL, round-bottomed flask, which was then cooled in a water bath. Aluminum amalgam (300 mg) was freshly prepared based upon a literature procedure[22] and was added right away to the precooled solution of saturated aldehyde. The resulting suspension was stirred vigorously for 1 h at ambient temperature. The reaction mixture was then filtered through a Celite pad (3 cm × 1 cm) with a filter paper on top, eluting with MeOH (50 mL). All the solvent was removed under vacuo. The organic residue was redissolved in CH_2Cl_2. TsCl (295 mg, 1.55 mmol, 1.5 equiv) was then added, followed by Et_3N (215 μL, 1.55 mmol, 1.5 equiv). The solution was allowed to stand at ambient temperature for 1 h and then concentrated under vacuo. The residue was purified by column chromatography (SiO_2, 30 mm × 20 cm, hexane/EtOAc, 10/1, 4/1) to give 311 mg of **23a** as a colorless, heavy oil. The product was crystallized from EtOH to afford 269 mg (82%) of an analytically pure white solid. Data for **23a**: mp (sealed tube) 99.5−100.5 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (m, 2 H, HC(12)), 7.34−7.18 (m, 7 H, aromatic H's), 3.68 (m, 1 H, HC(1)), 3.58 (m, 1 H, HC(6)), 3.15 (m, 1 H, HC(6′)), 2.96 (m, 2 H, HC(1′), HC(2)), 2.41 (s, 3 H, HC(15)), 2.05−1.92 (m, 2 H, HC(3), HC(5)), 1.91 (m, 1 H, HC(4)), 1.79−1.61 (m, 3 H, HC(3′), HC(4′), HC(5′)); ^{13}C NMR (126 MHz, $CHCl_3$): δ 144.3 (C(7)), 142.9 (C(11)), 136.4 (C(20)), 129.6 (C(13)), 128.6 (C(9)), 127.2 (C(8)), 126.9 (C(12)), 126.5 (C(10)), 54.5 (C(1)), 48.2 (C(6)), 47.7 (C(2)), 35.0 (C(3)), 28.8 (C(5)), 25.4 (C(4)), 21.5 (C(15)); IR ($CDCl_3$): cm^{-1} 3156 (w), 2937 (m), 2360 (s), 2342 (s), 1794 (w), 1600 (m), 1459 (m), 1382 (w), 1336 (s), 1159 (s), 1092 (m), 1047; TLC R_f 0.36 (hexane/EtOAc, 3/1) [silica gel, UV, I_2, CAM]. Anal. Calcd for $C_{19}H_{23}NO_2S$: C, 69.27; H, 7.04; N, 4.25. Found: C, 69.17; H, 7.20; N, 4.38.

Acknowledgment. We are grateful to the National Institutes of Health for generous financial support (GM R01-30938).

Supporting Information Available: Full experimental procedures and characterization data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO071126I

(22) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1345−1353.