solution was stirred at −78 °C for 4 h, quenched with 0.3 mL of saturated sodium bicarbonate solution, diluted with ethyl acetate, dried, and concentrated in vacuo. Benzene was added and the solution was again concentrated in vacuo. The residue was dissolved in methylene chloride (10 mL) and cooled to 0 °C. Pyridine (0.5 mL), acetic anhydride (0.15 mL), and DMAP (1 mg) were then added and the solution was allowed to slowly warm to room temperature overnight. The solution was concentrated in vacuo, ether (30 mL) was added, and the organic layer was extracted with copper sulfate solution. The organic layer was dried, concentrated in vacuo, and purified by chromatography using hexanes/ethyl acetate. The purification afforded 9 mg (55% yield).

1b: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.74 (s, 3 H), 1.75 (br s, 3 H), 2.03 (s, 3 H), 2.06 (s, 3 H), 2.11 (s, 3 H), 2.16 (s, 3 H), 2.82 (d, J = 4 Hz, 1 H), 3.07 (d, J = 4 Hz, 1 H), 3.85 (d, J = 5 Hz, 1 H), 4.08–4.18 (m, 2 H), 4.35 (d, J = 12 Hz, 1 H), 5.18–5.22 (m, 1 H), 5.72–5.80 (m, 1 H), 5.82 (d, J = 3 Hz, 1 H); IR ($CDCl_3$ solution) 1740, 1438, 1220 cm^{-1}; MS, m/e 107, 122, 164, 181, 218, 229, 248, 275, 320, 367, 409, 427, 469, 470; HRMS, m/e for $C_{21}H_{23}D_3O_8$ (M^+ − HOAc) calcd 409.18161, found 409.18165.

Acknowledgment. We thank the U.S. Army Medical Research Institute for financial support through contract DAMD17-85-C-5008.

Registry No. **1a**, 112841-34-6; **1b**, 112818-29-8; **1b** (3,4,15-triacetate), 112818-32-3; **2**, 2270-40-8; **2** (triacetate), 4297-61-4; **8a-3**, 112818-25-4; **8β-3**, 112818-30-1; **3** (X = H, H; Y = H), 105669-62-3; **4**, 112818-26-5; **5**, 112818-27-6; **5** (triol), 112818-31-2; **6**, 112818-28-7.

Cycloaddition Reactions of Bridgehead Enones

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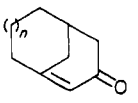
The cycloaddition reactions of bridgehead enones derived in situ from ketones **8**, **9**, and **10** with various dienes at 0 °C afford good yields of adducts. Even 1,1,3-trisubstituted dienes work well. The exclusive exo stereochemistry can be rationalized in terms of a stepwise mechanism involving ionic intermediates.

The synthesis of molecules containing a combination of fused and bridged rings has been a longstanding problem in organic synthesis. Most strategies for a compound such as **1** are linear and involve the construction of a fused tricyclic intermediate such as **2** followed by the appendage of the two-carbon bridge. One advantage of this strategy is that many routes to compounds such as **2** have already been worked out.[1] A clear disadvantage is the linear approach. A quite different strategy would involve the connection of **3** and **4** to produce **1** (Scheme I). This strategy is both convergent and flexible. It requires, however, bond formation to a bridgehead carbon atom, a process that has been relatively little studied.[2]

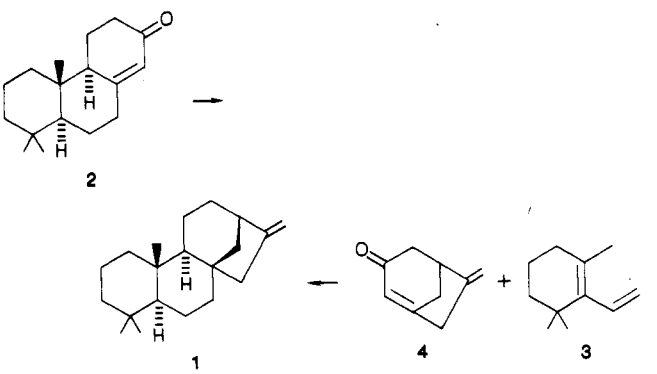
Bridgehead carbon–carbon bond formation is complicated by the high reactivity of bridgehead intermediates. Bridgehead anions, carbocations, and radicals are all more reactive than their acyclic counterparts. Double bonds at a bridgehead are also reactive, but not as reactive as bridgehead enones such as **5**. These bridgehead enones



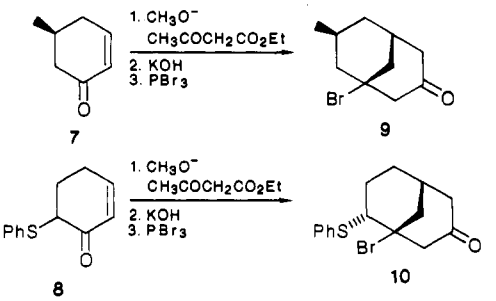
5 (n = 1, 2)

are extremely unstable. Calculations using Allinger's MM2 program indicate that the bridgehead alkene is twisted from planarity by approximately 25°.[3] This twist greatly enhances the inherent electrophilicity of the enone subunit. Alcohols and amines add readily at ambient temperature.[4]

Scheme I



Scheme II



In the absence of nucleophiles, the bridgehead enone dimerizes. Recently, House and Trahanovsky have demonstrated that enone **5** (n = 1) when produced by flash vacuum pyrolysis is stable in solution at −78 °C.[5]

In addition to our own work, the trapping of bridgehead enones with dienes has been accomplished by Magnus and by House.[6] We were the first to demonstrate the regio-

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(2) Kraus, G. A.; Hon, Y.-S. *J. Org. Chem.* **1985**, *50*, 4605. Shea, K. J. *Tetrahedron* **1980**, *36*, 1683.
(3) House, H. O.; Outcalt, R. J.; Haack, J. L.; VanDerveer, D. *J. Org. Chem.* **1983**, *48*, 1654.
(4) Bestmann, H. J.; Schade, G. *Tetrahedron Lett.* **1982**, *23*, 3543. Kraus, G. A.; Hon, Y.-S. *J. Am. Chem. Soc.* **1985**, *107*, 4341.
(5) Campbell, K. A.; House, H. O.; Surbur, B. A.; Trahanovsky, W. S. *J. Org. Chem.*, submitted for publication.

0022-3263/88/1953-1397$01.50/0

Scheme III

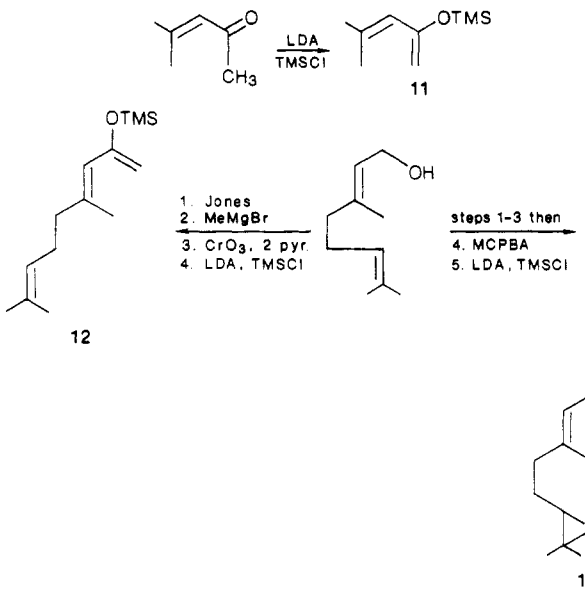
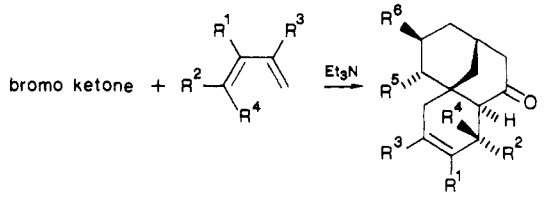
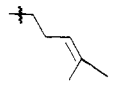
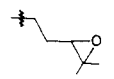
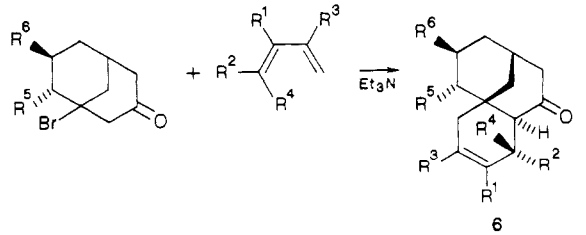


Table I



ketone	R^1	R^2	R^3	R^4	% yield of 6	
10	$(CH_2)_4$		OTMS	H	97	15
9	$(CH_2)_4$		OTMS	H	52	16
10	H	H_3CO	OTMS	H	98	17
10	H	OAc	H	H	63	18
10	H	H	H	H	41	19
9	H	OAc	H	H	55	20
10	H	CH_3	OTMS	CH_3	46	22
10	H		OTMS	CH_3	46	23
10	H		OTMS	CH_3	81	24

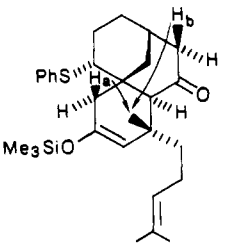
and stereoselectivity of the addition with unsymmetrical dienes. Unexpectedly, the exo adduct **6** was the exclusive



product. We have since studied several more dienes, including 1,1,3-trisubstituted ones, and now report our results of this study plus a working hypothesis to explain the unusual stereoselectivity.

The bromo ketone precursors to the bridgehead enones were synthesized as shown in Scheme II. Compounds **9**[8] and **10** were prepared from the corresponding cyclohexenones **7** and **8** by treatment with ethyl acetoacetate, decarbalkoxylation with KOH, and bromide formation with PBr_3. Most of the dienes used in this study were prepared from the parent ketones with LDA and trimethylchlorosilane. Scheme III shows the synthesis of **11**,[9] triene **12**,[10] and the epoxy diene **13**.

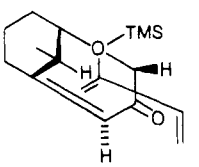
The bridgehead enones were formed in situ with triethylamine in methylene chloride. In all cases only a two- or fourfold excess of diene was used. The adducts are collated in Table I. It is clear that even 1,1,3-trisubstituted dienes such as **11–13** form adducts in good yields with high stereoselectivity. Initially, the assignment of stereochemistry of adducts **23** and **24** presented a problem, because



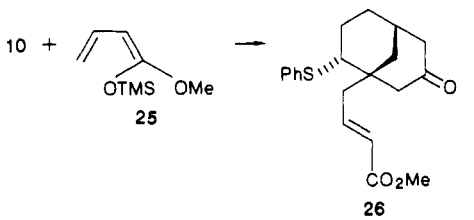
they did not contain the vicinal methine subunit that had enabled us to characterize adducts **18**, **19**, and **20**.

The assigned structure **23** is supported by NOESY and COSY NMR experiments. With the COSY experiment, H_a and H_b were identified. Both H_a and H_b showed significant interactions with the methyl group as evidenced by the NOESY NMR experiment.

The exclusive preference for the exo mode of addition rather than the endo mode is surprising. The general preference for the endo mode of addition in most intermolecular Diels–Alder reactions stems from the stabilization of the endo mode by secondary orbital overlap.[11] As the figure depicted below indicates, such overlap would



be difficult, if not impossible, in our cases. There also remains the question of whether the reaction proceeds via ionic intermediates, a possible consequence of the increased electrophilicity of the bridgehead enones. One reaction which may bear on this question is the reaction of ketene acetal **25** with ketone **10**. In this case the unsaturated



ester **26** was formed in 78% yield. Fragmentation of an initially formed adduct could also explain the observed

(6) Magnus, P.; Gallagher, T.; Brown, P.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2105. House, H. O.; DeTar, M. B.; VanDerveer, D. *J. Org. Chem.* **1979**, *44*, 3793. Kraus, G. A.; Hon, Y.-S. *J. Org. Chem.* **1986**, *51*, 116.

(7) Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655.

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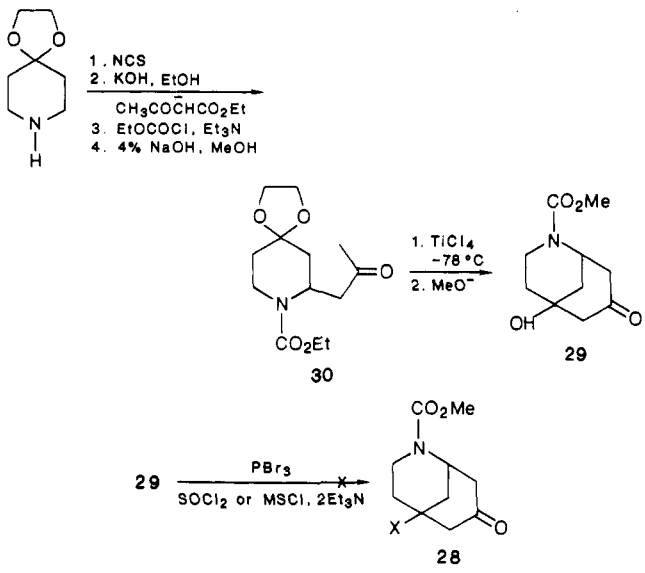
(9) Casey, C. P.; Jones, C. R.; Tukada, H. *J. Org. Chem.* **1981**, *46*, 2089.

(10) The ketone has been prepared: Buchi, G.; Pickenhagen, W. *J. Org. Chem.* **1973**, *38*, 894.

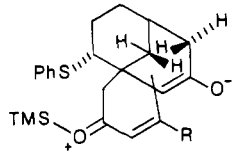
(11) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 4388.

(12) Node, M.; Sai, M.; Fujita, E.; Juki, K. *Heterocycles* **1984**, *22*, 1701.

Scheme IV

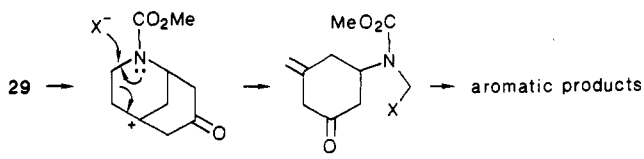


product. However, no fragmentation was observed with adduct **18**. Additionally, the facile formation of adducts from dienes **11–13** at 0 °C would be more readily explained by ionic intermediates. These dienes all contain a methyl group which inhibits the *s*-cis form of the planar diene. Generally, such a substituent renders the diene unreactive in cycloadditions. However, the methyl group would have little effect if an ionic addition was involved. Moreover, the exo stereochemistry could then be explained as illustrated below. The enolate would be expected to trap the



allylic cation so as to minimize nonbonded interactions between the two axial hydrogens on the bicyclo[3.3.1]nonane unit and the incoming electrophile.

We next considered bridgehead enone formation via compound **28**. Substitution at the bridgehead carbon would create a flexible route to morphinans. The hydroxy ketone **29** was prepared as described in Scheme IV. The commercially available ketal amine was converted into an imine which was treated with the sodium salt of ethyl acetoacetate and then protected as carbamate **30**. Ketal hydrolysis followed by cyclization afforded **29**. The carbamate-protecting group had been selected to prevent amine participation in undesired fragmentation reactions. Unfortunately, all attempts to activate the hydroxyl group (PBr_3, ether; $SOCl_2$, CH_2Cl_2; MsCl, $2Et_3N$) led to the unraveling of the bicyclic system presumably via the mechanism shown below.



In summary, the Diels–Alder reactions of bridgehead enones provides a rapid entry to bridged tricyclic systems. Some of these systems such as **24** have functionality suitable for the eventual elaboration into biologically active kaurenoid diterpenes. Adduct **21** may be a useful intermediate for the synthesis of the recently isolated isocedrenes. The Diels–Alder reactions are highly stereoselective, affording only exo adducts. Whatever the mechanism by which the adducts are actually formed, the high stereoselectivity will be a useful synthetic advantage.

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. Dichloromethane was distilled from phosphorus pentoxide. Infrared spectra were determined on a Perkin-Elmer 1320 spectrometer. Nuclear magnetic resonance spectra were determined on a Varian EM 360 60-MHz instrument and on a Nicolet 300-MHz instrument. Carbon-13 NMR spectra were determined on a JEOL FX-90Q Fourier transform instrument. High resolution mass spectra were determined on a Kratos mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

Diels–Alder Reactions for Adducts 15–20. To a solution of the bridgehead bromide (1 equiv) and the diene (2 equiv) in methylene chloride (1 mL/mmol bromide) at 0 °C was added dropwise triethylamine (2 equiv). The solution was allowed to warm to ambient temperature. The reaction was diluted with water and extracted with methylene chloride. The crude product was chromatographed on silica gel.

Diels–Alder Reactions for Adducts 22–24. To a mixture of the bridgehead bromide (1 equiv) and the diene (2–4 equiv) at 0 °C was added dropwise triethylamine (1.2 equiv). The solution was allowed to warm to ambient temperature slowly over 4 h. The precipitate (Et_3N–HBr) was then filtered through glass wool and the concentrate chromatographed on silica gel by using hexanes/ethyl acetate.

1-Bromo-8-(phenylthio)bicyclo[3.3.1]nonan-3-one (10). To a freshly prepared solution of sodium methoxide (27.3 mmol) in 300 mL of methanol were added ethyl acetoacetate (3.56 g, 27.3 mmol) and **8** (5.07 g, 24.9 mmol). The reaction was heated at 65 °C for 3 days. The solution was cooled and concentrated, and the resulting oil was dissolved in 30 mL of methanol and 10 mL of water containing KOH (1.4 g, 24.9 mmol). The solution was heated under reflux for 12 h. The solution was cooled and the solvents were removed in vacuo. The residual aqueous solution was extracted three times with CH_2Cl_2. The organic layer was dried and concentrated. The crude product was purified by flash chromatography using 3:1 hexanes/ethyl acetate to afford a 54% yield of hydroxy ketone. To a solution of this ketone (46.3 g, 176.8 mmol) in 250 mL of ether at 25 °C was added dropwise PBr_3 (18.3 mL, 194.5 mmol). The solution was stirred at 25 °C for 6 h. It was poured into ice and then extracted with CH_2Cl_2. The organic layer was dried and concentrated. The crude product was purified by silica gel chromatography using 4:1 hexanes/ethyl acetate to afford 38.90 g (68% yield) of **10**. This was a 6:1 mixture of diastereomers. The major one crystallized: 300-MHz ^1H NMR ($CDCl_3$) 1.40–1.95 (m, 4 H), 2.34–2.94 (m, 7 H), 3.50–3.59 (m, 1 H), 7.23–7.32 (m, 3 H), 7.48–7.52 (m, 2 H); IR (CH_2Cl_2) 1718, 1266, 732 cm^{-1}; ^{13}C NMR ($CDCl_3$) 29.85, 31.56, 45.07, 46.39, 58.71, 61.39, 65.99, 127.59, 128.89, 133.25, 134.26, 206.46.

Adduct **15**, colorless oil with R_f 0.63 in 3:1 hexanes/ethyl acetate: 300-MHz ^1H NMR ($CDCl_3$) 0.20 (s, 9 H), 1.02–1.90 (m, 12 H), 2.02–2.17 (m, 6 H), 2.67–3.06 (m, 4 H), 7.02–7.14 (m, 3 H), 7.18–7.24 (m, 2 H); IR (CH_2Cl_2) 29.35, 1700, 1266, 1181, 842, 740 cm^{-1}; ^{13}C NMR ($CDCl_3$) 0.52, 26.99, 27.64, 28.22, 29.33, 33.49, 33.75, 37.65, 39.21, 40.25, 40.58, 46.89, 51.18, 60.09, 114.97, 126.74, 128.82, 131.75, 135.91, 137.93, 214.28. Anal. Calcd for $C_{26}H_{36}SiSO_2$: C, 70.86; H, 8.23. Found C, 70.90; H, 8.41.

Adduct **16**, colorless, viscous oil with R_f 0.76 in 3:1 hexanes/ethyl acetate: 300-MHz ^1H NMR ($CDCl_3$ 0.15 (s, 9 H), 0.80 (d, J = 6 Hz, 3 H), 0.83–1.52 (m, 12 H), 1.58–2.00 (m, 8 H), 2.14–2.90 (m, 2 H); IR (CCl_4) 2940, 1702, 1257, 1200, 1172, 1008, 892 cm^{-1}; mass spectrum, m/e 73, 181, 199, 256, 289, 328, 346; HRMS, m/e calcd 346.2328, found 346.2327.

Adduct **19**, colorless oil with R_f 0.55 in 3:1 hexanes/ethyl acetate: ^1H NMR ($CDCl_3$) 1.15–2.47 (m, 11 H), 2.52–3.25 (m, 4 H), 5.60 (br s, 2 H), 7.05–7.45 (m, 5 H); IR (CH_2Cl_2) 2936, 1710, 1586, 1270, 740 cm^{-1}; mass spectrum, m/e 67, 79, 91, 110, 129, 147, 170, 189, 200, 298; HRMS, m/e calcd 298.1391, found 298.1392.

Adduct **17**, yellow oil with R_f 0.19 in 3:1 hexanes/ethyl acetate: 300-MHz ^1H NMR ($CDCl_3$) 0.15 (s, 9 H), 1.50–1.72 (m, 4 H), 1.82–2.05 (m, 2 He, 2.24–2.32 (m, 3 H), 2.67–3.06 (m, 4 H), 3.20

(s, 3 H), 4.00–4.03 (m, 1 H), 5.16 (d, J = 5 Hz, 1 H), 7.20–7.29 (m, 3 H), 7.37–7.40 (m, 2 H); IR (film) 2940, 1702, 1270, 1190, 1082, 890, 852, 740 cm^{-1}; ^{13}C NMR ($CDCl_3$) 0.29, 28.33, 29.49, 33.34, 38.48, 39.49, 41.11, 46.85, 52.73, 56.40, 60.19, 77.48, 100.24, 126.86, 128.83, 132.10, 135.56, 152.92, 212.66; mass spectrum, m/e 73, 85, 110, 161, 233, 275, 307, 366, 385, 416; HRMS, m/e calcd 416.1841, found 416.1845.

Adduct **18**, clear oil with R_f 0.36 in 3:1 hexanes/ethyl acetate: 300-MHz ^1H NMR ($CDCl_3$) 1.30–1.75 (m, 3 H), 1.90–2.10 (m, 2 H), 1.99 (s, 3 H), 2.25–2.75 (m, 4 H), 2.92–3.15 (m, 4 H), 5.38–5.44 (m, 1 H), 5.85–6.00 (m, 2 H), 7.21–7.30 (m, 3 H), 7.36–7.40 (m, 2 H); IR (CH_2Cl_2) 2936, 1735, 1700, 1230, 1013, 935, 730 cm^{-1}; ^{13}C NMR ($CDCl_3$) 21.13, 28.03, 29.07, 33.10, 36.09, 37.13, 46.37, 51.24, 59.63, 67.76, 122.13, 127.00, 128.89, 130.52, 132.08, 135.07, 169.08, 211.28; mass spectrum, m/e 91, 145, 168, 187, 278, 296, 356; HRMS, m/e calcd 356.1446, found 356.1451.

Adduct **20**, light yellow oil: 300-MHz ^1H NMR 0.85 (d, J = 6 Hz, 3 H), 1.01–1.23 (m, 3 H), 1.38–1.72 (m, 2 H), 1.85–2.10 (m, 3 H), 2.01 (s, 3 H), 2.32–2.68 (m, 5 H), 5.32–5.38 (m, 1 H), 5.76–5.94 (m, 2 H); IR ($CDCl_3$) 2920, 1735, 1700, 1320, 1240, 910, 730 cm^{-1}; ^{13}C NMR ($CDCl_3$) 21.13, 22.57, 24.45, 29.91, 32.45, 33.95, 38.82, 41.16, 46.95, 50.59, 56.19, 67.18, 122.32, 129.80, 169.01, 212.26; mass spectrum, m/e 91, 117, 145, 158, 202, 219, 262; HRMS, m/e calcd 262.1569, found 262.1568.

Adduct **22**, clear viscous oil with R_f 0.46 in 4:1 hexanes/ethyl acetate: 300-MHz ^1H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 1.66 (br s, 6 H), 1.80–2.40 (m, 10 H), 2.75 (d, J = 8 Hz, 1 H), 3.14–3.22 (m, 1 H), 3.34 (br s, 1 H), 5.40 (br s, 1 H), 7.15–7.42 (m, 5 H); mass spectrum, m/e 73, 193, 263, 305, 399, 414; HRMS, m/e calcd 414.20528, found 414.20489.

Adduct **23**, light yellow oil with R_f 0.35 in 5:1 hexanes/ethyl acetate: ^1H NMR ($CDCl_3$) δ 0.23 (s, 9 H), 1.32 (s, 3 H), 1.1–3.3 (m, 23 H), 5.18 (m, 1 H), 5.42 (br s, 1 H), 7.15–7.65 (m, 5 H); IR (film) 1700, 1435, 1248, 840 cm^{-1}; mass spectrum, m/e 75, 223, 241, 283, 347, 392, 467, 482.

Adduct **24**, clear oil with R_f 0.43 in 4:1 hexanes/ethyl acetate: ^1H NMR ($CDCl_3$) δ 0.22 (s, 9 H), 1.30 (s, 3 H), 1.05–3.2 (m, H), 5.36 (br s, 1 H), 7.05–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 2.47, 18.60, 24.71, 26.60, 27.96, 29.46, 30.82, 33.17, 33.75, 34.01, 36.94, 39.60, 39.93, 41.23, 46.30, 58.01, 60.15, 60.61, 63.53, 72.83, 114.78, 126.81, 127.98, 128.24, 128.76, 132.01, 134.87, 135.59, 210.96; IR (film) 1700, 1248, 840, 780 cm^{-1}; HRMS, m/e calcd 498.2624, found 498.2619.

Adduct **26**: 300-MHz ^1H NMR ($CDCl_3$) δ 1.24 (5, J = 7 Hz, 3 H), 1.38–3.00 (m, 14 H), 4.18 (q, J = 7 Hz, 2 H), 5.86 (d, J = 13 Hz, 1 H), 6.94 (dt, J = 12 Hz, 6 Hz, 1 H), 7.12–7.26 (m, 3 H), 7.32–7.40 (2 H); IR (film) 2960, 1722, 1705, 1330, 915 cm^{-1}; MS, m/e 91, 158, 313, 358.

Synthesis of Ketone 30. To a vigorously stirred suspension of NCS (1.87 g, 14 mmol) in dry ether (14 mL) which had been cooled to −8 °C (ice–NaCl bath) was added dropwise the piperidino ketal (1.79 mL, 14 mmol). The mixture was stirred for 1 h and then was warmed to ambient temperature and stirred for an additional 3 h. The filtrate was washed with brine and then concentrated in vacuo to approximately 5 mL. This concentrated solution was taken directly on to the next step.

The concentrated solution (assumed to contain 14 mmol of N-chloro product) was added dropwise to a solution of KOH (1.02 g) in absolute EtOH (9 mL) which had been cooled to 4 °C (ice–NaCl bath). The ice was allowed to melt as the reaction warmed to ambient temperature over 3 h. The reaction mixture was then filtered into a solution of the sodium salt of ethyl acetoacetate (from NaH in ether). The ether was removed and the ethanolic solution was then heated at reflux overnight. The crude reaction mixture was cooled and filtered. The filtrate was concentrated in vacuo. This oil was diluted with water and extracted 3× with methylene chloride. The dried organic layer was concentrated and chromatographed to provide a 30% yield (from the amino ketal) of product. This product was routinely protected as the carbamate as soon as possible.

The keto amine (0.102 g, 0.51 mmol), ethyl chloroformate (0.2 mL, 2 mmol) and potassium carbonate (0.424 g, 3.07 mmol) were heated to reflux in acetone (2 mL) for 14 h. The filtrate was concentrated in vacuo, dissolved in MeOH containing NaOH, stirred for 2 h, diluted with water, and extracted with methylene chloride. The crude product was purified by chromatography.

Keto acetal 30: ^1H NMR ($CDCl_3$) δ 1.28 (t, J = 7 Hz, 3 H), 1.5–1.95 (m, 4 H), 2.22 (s, 3 H), 2.50–3.45 (m, 2 H), 3.96 (br s, 4 H), 4.16 (q, J = 7 Hz, 2 H), 4.6–5.0 (m, 3 H); mass spectrum, m/e 56, 70, 86, 99, 198, 214, 271.

Synthesis of Ketol 29. To a solution of **30** (1.6 g, 6.2 mmol) in dry methylene chloride (25 mL) at −78 °C was added dropwise $TiCl_4$ (2.92 mL, 25 mmol). The resulting brick-red mixture was stirred at −78 °C until TLC indicated that **30** had been consumed (approximately 1 h). The mixture was then cautiously quenched with aqueous sodium bicarbonate and extracted with methylene chloride. The organic layer was washed with brine, dried, and concentrated. The crude product was purified by chromatography on silica gel using 2:1 ethyl acetate/hexanes.

The resulting diketone (1.00 g, 4.69 mmol) in methanol (7 mL) was added to a solution of NaOMe (prepared from 5.6 mmol of Na) in MeOH (38 mL) at 0 °C. The solution was then stirred for 1 h, diluted with water, and neutralized to pH 7 with 1 N HCl. The solution was then extracted with methylene chloride, dried, and concentrated to afford 0.740 g of **29** (60% overall from **30**).

Keto alcohol 29: 300-MHz ^1H NMR ($CDCl_3$) δ 1.70–2.30 (m, 4 H), 2.45–2.70 (m, 2 H), 3.4–3.8 (m, 3 H), 3.72 (s, 3 H), 4.02–4.10 (m, 1 H), 4.46 (br s, 1 H), 4.60 (br s, 1 H); IR ($CHCl_3$) 3580, 3440, 1735, 1685, 1450, 1392, 1114, 907 cm^{-1}; HRMS, m/e 55, 71, 85, 149, 163, 181, 195, 213.

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Registry No. **7**, 7214-50-8; **8**, 88354-73-8; **9**, 66318-41-0; **10**, 99656-33-4; **11**, 6651-46-3; **12**, 113109-13-0; **13**, 113109-14-1; **15**, 99656-27-6; **16**, 99656-28-7; **17**, 99656-30-1; **18**, 99656-31-2; **19**, 99656-29-8; **20**, 99656-32-3; **22**, 113109-15-2; **23**, 113109-16-3; **24**, 113109-17-4; **25**, 85636-50-6; **26**, 113109-18-5; **29**, 113109-19-6; **30**, 113109-20-9; AcH_2COOEt, 141-97-9; $Me_2C{=}CHCOMe$, 141-79-7; $HOCH_2CH{=}C(Me)(CH_2)_2CH{=}CMe_2$, 624-15-7; $CH_2{=}C(OTMS)CH{=}CHOMe$, 59414-23-2; $AcOCH{=}CHCH{=}CH_2$, 1515-76-0; $CH_2{=}CHCH{=}CH_2$, 106-99-0; $AcCH^-COOEt{\cdot}Na$, 19232-39-4; *endo*-1-hydroxy-8-(phenylthio)bicyclo[3.3.1]nonan-3-one, 113109-21-0; 1-[1-(trimethylsilyloxy)ethene]cyclohexene, 54781-35-0; 1,4-dioxa-8-azaspiro[4.5]decane, 177-11-7; 7-(2-oxopropyl)-1,4-dioxa-8-azaspiro[4.5]decane, 113109-23-2; ethyl 4-oxo-2-(2-oxopropyl)-1-piperidinecarboxylate, 113109-22-1.

Supplementary Material Available: Complete data for the COSY and NOESY experiments for adduct **24** (2 pages). Ordering information is given on any current masthead page.