J = 7.8, 1 H). EIMS: 349* (M^+, 1), 290* (1), 272* (1), 233* (2), 220* (4), 141 (4), 111 (5), 43 (100). HRMS: 348.9622; calcd for $C_{11}H_{12}BrNO_5S$, 348.9618.

Alkaline Permethylation of Mercapturic Acids. A mixture of compounds **2–4** (0.95 mg, 3 μmol each) was dissolved in 1.5 mL of water in a 13 × 100 mm culture tube and purged briefly with nitrogen. A 3-g sample (21.7 mmol) of solid K_2CO_3 and 0.5 mL (8.0 mmol) of CH_3I were then added, and the tube was sealed with a Teflon-lined screw cap. The tube was then immersed up to the level of the liquid meniscus in an oil bath kept at 130 °C behind a safety shield in a hood. The CH_3I (lower layer) refluxed vigorously, giving good mixing, while the upper portion of the culture tube served as an air-cooled condenser. After 5 h the oil bath was lowered away, the tube was allowed to cool and opened cautiously, and the contents were extracted with *n*-pentane (4 × 2 mL). After the volume of the extracts was adjusted and an internal standard (2,3-dichloronitrobenzene was convenient) was added, the yields of the bromothioanisole isomers were determined by reversed-phase HPLC with a C_8 column (10 μm, 4.6 × 250 mm) eluted with 50% methanol at 1.5 mL/min. On the basis of comparison to authentic standards, the retention times for *o*-, *p*-, and *m*-bromothioanisole were 19.2, 23.8, and 26.0 min, respectively. Peak integration, with correction for differences in absorption at 254 nm, indicated the yeilds of the three isomers were 76, 73, and 76%, respectively.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of compounds **13–17** and the methyl esters of compounds **18–20** and ^1H NMR spectrum of compound **21** (9 pages). Ordering information is given on any current masthead page.

Linearly Fused vs Bridged Regioselection in the Intramolecular 1,3-Diyl Trapping Reaction

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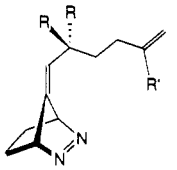
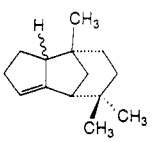
The intramolecular diyl trapping reaction can now be used to obtain synthetically useful quantities of either bridged or linearly fused cycloadducts in a *selective* manner and *by design*. Bridged cycloadducts arise by intercepting the triplet diyl, while linearly fused products can be produced from either the singlet or the triplet. When an electron-withdrawing group is attached to the diylophile, the singlet diyl leads selectively to fused cycloadducts. On the other hand, the presence of a large alkyl group attached to the internal carbon of the diylophile affords bridged cycloadducts selectively from cycloaddition with the triplet. Four diazenes, **4–7**, differing only in the electronic and steric properties of the substituent located on the internal carbon of the diylophile, were studied. The diyl trapping reactions were conducted using ca. 1 mM solutions of diazene in THF at reflux for periods of 3–4 h; cycloadduct yields ranged from 68% (beginning with the dimethyl ketal **7**) to 98% (from keto diazene **4**). To determine the origin of the bridged cycloadducts, the effect of oxygen upon the product distribution was examined. The results show that the rate of the intramolecular triplet diyl cycloaddition is slower than the rate of the intermolecular reaction of the triplet with oxygen. The rate of triplet intramolecular cycloaddition can be *estimated* to be less than 4×10^6 to 4×10^7 s^{-1}.

Introduction

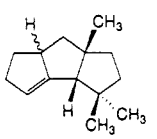
Several years ago, we became intrigued by the observation that unlike all previously conducted intramolecular diyl trapping reactions, the major product produced in the cycloaddition of the diyl derived from diazene **1** was the bridged (**2**), rather than the linearly fused regioisomer (**3**).[3] We were particularly interested in learning how to obtain *either* product *selectively*, and *by design*. That objective has been achieved and the results of our investivation are described below.



1, R = R' = CH_3
4, R = H, R' = $COCH_3$
5, R = H, R' = CH_2OH
6, R = H, R' = $CH(OCH_3)_2$
7, R = H, R' = $CCH_3(OCH_3)_2$



2



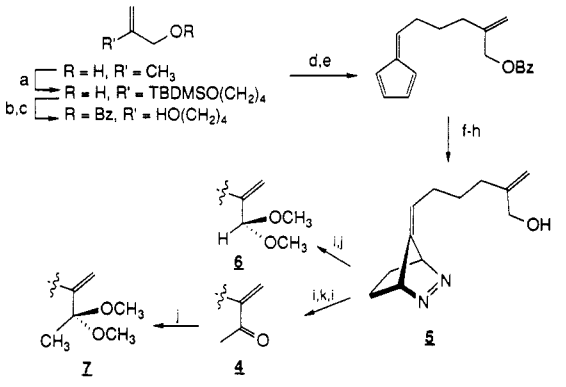
3

(1) Taken, in part, from the Ph.D. Dissertation of M.R.M., UCSB, 1989.

(2) In part; I.D.D. began study of the chemistry of diazene **5**: Dannecker-Doerig, I. M.S. Dissertation, UCSB, 1985.

(3) (a) Little, R. D.; Carroll, G. L.; Petersen, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 928. (b) Little, R. D. *Chem. Rev.* **1986**, *86*, 875. (c) the linearly fused tricyclopentanoids invariably display a signal at ca. 3.1 ppm which is characteristic for the hydrogen located at the A,B ring junction.

Scheme I. Preparation of Diazenes[a]



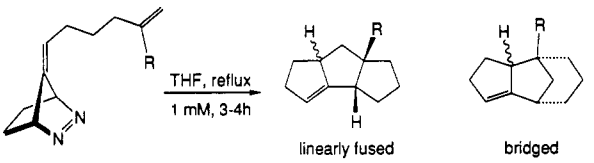
[a] (a) *n*-BuLi, TMEDA, −78 to 25 °C, 17 h; $Br(CH_2)_3OTBDMS$, THF, −78 °C, 10 min, 78%; (b) BzCl py, DMAP, CH_2Cl_2, 0–25 °C, 1 h, 96%; (c) HF, CH_3CN, 25 °C, 2.5 h, 96%; (d) PCC, Celite, CH_2Cl_2, 25 °C, 2 h, 85%; (e) CpH, Et_2NH, CH_3OH, 0–25 °C, 2.5 h; HOAc, 91%; (f) $(NCO_2Me)_2$, CH_2Cl_2, 4 °C, 8 h; (g) $(NCO_2K)_2$, HOAc, CH_2Cl_2, 0 °C, 1.5 h, 94% (two steps); (h) KOH, EtOH, reflux, 1.5 h; $K_3Fe(CN)_6$, H_2O, 0 °C, 97%; (i) Dess–Martin periodinane, CH_2Cl_2, 97%; (j) $HC(OCH_3)_3$, PPTS, CH_3OH; (k) MeLi, Et_2O, −78 °C, 74%.

Synthesis of Diyl Precursors

Four diazenes, **4–7**, differing only in the electronic and steric properties of the substituent located on the internal carbon of the diylophile, were studied. Each was syn-

0022-3263/90/1955-2742$02.50/0

Table I. Regioselectivity as a Function of the Electronic and Steric Demands of R



diazene	R	yield, %	linear/bridged	CA/CS[c] (fused)	exo/endo (bridged)
4	$COCH_3$	98	7.3:1	36.4:1	1.7:1
5	CH_2OH	91	1:1.9	13.2:1	1:1.3
6	$CH(OCH_3)_2$	86[a]	1:2	CA only	1:1.4
7	$CCH_3(OCH_3)_2$	68[b]	1:15.7	CA only	1.1:1

[a] Acetalization and diyl trapping. [b] Diyl trapping and conversion of ketal to carbonyl. [c] cis,anti/cis,syn.

thesized from 2-methyl-1-hydroxy-2-propene in accord with the sequence outlined in Scheme I.

Results

The intramolecular diyl trapping reactions were conducted using ca. 1 mM solutions of diazene in THF at reflux for periods of 3–4 h; cycloadduct yields ranged from 68% (beginning with the dimethyl ketal **7**) to 98% (from keto diazene **4**). Since the ketal cycloadducts partially convert to the corresponding carbonyl compound on chromatography, each was deliberately converted to the corresponding ketone to facilitate isolation; the yield, therefore, reflects the two-step process. The results are summarized in Table I.

To confirm the structure of the bridged cycloadducts, we compared the spectral and gas chromatographic characteristics of hydrocarbons **9** and **11**, obtained as illustrated in Scheme II from commercially available *exo*-tricyclo[5.2.1.$0^{2,6}$]decan-8-one (**8**) and independently synthesized *endo*-tricyclo[5.2.1.$0^{2,6}$]decan-8-one (**10**), with those obtained by degradation of alcohol cycloadducts **12** and **13**.[4a-f] Once these structures were secured, assignments for the bridged adducts obtained from ketone **4**, acetal **6**, and ketal **7** followed readily: the exo and endo bridged ketones **16** were converted to hydrocarbons **9** and **11**, the ketals **15** were converted to ketones **16**, and the bridged acetals **14** were transformed to alcohols **12** and **13**.

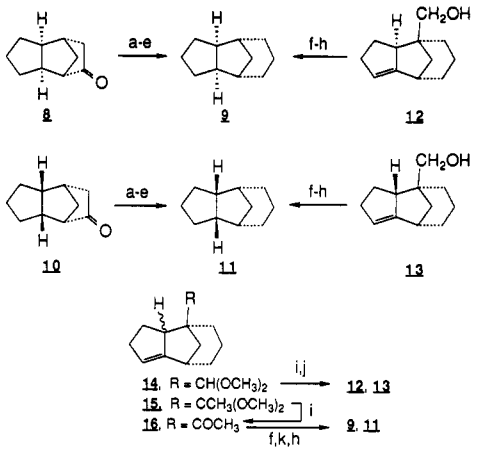
The linearly fused cycloadducts were identified by comparison of their spectral data with those of the many similar compounds previously prepared in these laboratories.[1-3] ^1H NMR spectra proved particularly useful as each of the linearly fused compounds displays a characteristic signal at ca. 3.1 ppm corresponding to the allylic bridgehead proton.

Examination of Table I reveals that the preference for formation of bridged cycloadducts varies depending upon the nature of the substituent attached to the internal carbon of the diylophile: an electron-withdrawing group leads preferentially to linearly fused cycloadducts, while an alkyl substituent affords varying degrees of bridged selectivity depending upon the size of the group (vide infra).

Origin of Bridged Cycloadducts. To determine the origin of the bridged cycloadducts, we examined the effect of oxygen on the product distribution obtained from diazene **5** (R = CH_2OH) and found that the bridged adducts, **12** and **13**, were no longer formed; in addition, the quantity of linearly fused cycloadduct decreased from 44% in the absence of oxygen to ca. 17% in its presence.[5] We suggest that, in analogy with the intermolecular diyl trapping reaction,[6] the bridged cycloadduct arises by trapping of the triplet diyl and that, in this case, the linearly fused product is formed by cycloaddition with both the singlet and triplet diyl.[7] The linearly fused cycloadduct produced when the reaction is conducted in the presence of oxygen reflects the amount which is formed from the singlet diyl. We conclude that, when an alkyl group is attached to the internal carbon of the diylophile, then both the singlet and the triplet forms of the diyl can participate in cycloaddition and that the bridged products arise by trapping the triplet.

Both the singlet and the triplet diyl *could* have undergone reaction with oxygen. If so, then the ca. 17% linearly fused cycloadduct remaining when the reaction was conducted in the presence of oxygen would not reflect

Scheme II. Determination of the Structure for Bridged Cycloadducts[a]



[a] (a) LDA, TMSiCl, THF, −78 °C, 3 h; (b) Zn(Ag), CH_2I_2, Et_2O, reflux, 18 h; py; (c) NaOH, MeOH, 4 °C, 18 h; (d) $HS(CH_2)_3SH$, BF_3-OEt_2, CH_2Cl_2, 25 °C, 21 h; (e) Ra-Ni, EtOH, 75 °C, 17 h; (f) H_2, PtO_2, 25 °C, 1 h; (g) $RuCl_3$, $NaIO_4$, $H_2O/CH_3CN/CCl_4$; (h) sodium salt of 2-mercaptopyridine *N*-oxide, DMAP; *t*-BuSH, PhH, reflux; (i) PPTS, H_2O/acetone; (j) $LiAlH_4$, Et_2O, 0 °C; (k) KI, I_2, dioxane/H_2O.

(4) (a) Stothers, J. B.; Patel, H. A.; Jarline, J. L. *Can. J. Chem.* **1984**, 1159. (b) Stothers, J. B.; Ragauskas, A. J. *Can. J. Chem.* **1984**, 250. (c) Cheng, A. K.; Ghosh, A. K.; Stothers, J. B. *Can. J. Chem.* **1984**, 1385. (d) Patel, V.; Ragauskas, A. J.; Stothers, J. B. *Can. J. Chem.* **1986**, 1440. (e) Dawson, B. A.; Ghosh, A. K.; Jurlina, J. L.; Ragauskas, A. J.; Stothers, J. B. *Can. J. Chem.* **1984**, 2521. (f) Clements, M. T. M.; Klinck, R. E.; Peiris, S.; Ragauskas, A. J.; Stothers, J. B. *Can. J. Chem.* **1988**, 454.

(5) Oxygen derived products are formed in place of the bridged cycloadducts. See, for example: Little, R. D.; Losinski-Dang, L.; Venegas, M. G.; Merlic, C. *Tetrahedron Lett.* **1983**, *24*, 4499.

(6) (a) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York 1982; Chapter 4. (b) *Intermolecular* diyl trapping leads to bridged cycloadducts by forming two new sigma bonds between the diylophile and radical centers on the diyl ring. In contrast, *intramolecular* diyl trapping leads to bridged cycloadducts by forming one bond to a diyl–ring carbon and the other to the exocyclic radical center.

(7) We have recently been able to detect the triplet diyl derived from diazene **5** by ESR spectroscopy. We thank Dr. C. Fite for assistance with those experiments.

Table II. Results of Molecular Mechanics Calculations[11]

R	ring size	energy contributions to MME[a]						MME[b]	ΔMME[c]
		STR	BND	SB	TOR	VDW	DIP		
CH_2OH	five	1.05	9.07	−0.08	9.35	3.98	0.18	25.56	6.30
	six	0.71	7.14	−0.02	6.04	3.23	0.16	17.26	
$CH(OCH_3)_2$	five	1.93	13.50	0.29	12.66	7.67	0.77	36.82	10.85
	six	1.17	9.48	0.29	7.06	7.22	0.76	25.97	
$CCH_3(OCH_3)_2$	five	3.00	15.59	0.54	14.25	9.63	0.69	43.70	12.21
	six	1.76	10.52	0.35	8.70	8.48	0.67	30.49	

[a] STR = stretch, BND = bend, SB = stretch–bend, TOR = torsion, VDW = van der Waals, DIP = dipolar. [b] Molecular mechanics energy (MME; kcal/mol). [c] ΔMME = MME(5-membered ring) − MME(6-membered ring).

the amount of it produced from the singlet diyl in its absence. However, it is very unlikely that the singlet survives long enough to react with the estimated 10^{-2}–10^{-3} M concentrations of oxygen which are likely to be present in solution.[8] The triplet diyl **17-T**, on the other hand, lives for a comparitively long 900 ns and reacts with oxygen with a rate constant of 4.3×10^9 M^{-1} s^{-1}.[9] Assuming that the lifetime for **5-T** is comparable to that of **17-T**, then it clearly survives long enough to react with oxygen and account for the chemistry described above.

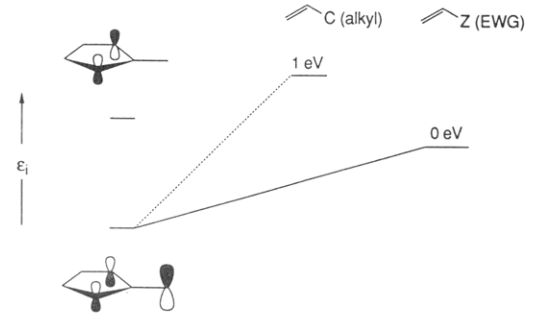
17-S,T

The results show that the rate of the *intramolecular triplet diyl cycloaddition* is slower than the rate of the *intermolecular* reaction of the triplet with oxygen. If the concentration of oxygen is indeed 10^{-2}–10^{-3} M, and the rate constant for the reaction of diyl **5-T** with oxygen is, like that for **17-T**, ca. 4×10^9 M^{-1} s^{-1}, then one can make the first *estimate* of the rate of triplet intramolecular cycloaddition to be less than 4×10^6 to 4×10^7 s^{-1}.[10]

When an electron-withdrawing substituent is attached to the internal carbon of the diylophile, as is the case for the diazene with R = CO_2CH_3, then conducting the diyl trapping reaction in the presence of oxygen affords, within experimental error, the same high yield of linearly fused cycloadducts (>96%) as was obtained in the absence of oxygen. Once again, however, no bridged products were formed. We conclude that the singlet diyl is the dominant reactive intermediate in this cycloaddition and suggest that linearly fused cycloadducts will be formed selectively via the singlet diyl whenever an electron-withdrawing group is attached to the diylophile. The chemistry of keto diazene **4** (R = $COCH_3$) is in full accord with these expectations (note Table I).

The effect of an electron-withdrawing group is to lower the energy of both the HOMO and the LUMO of the diylophile. In so doing, the diyl HOMO–diylophile LUMO energy gap is reduced, thereby leading to an increase in the rate of a diyl HOMO-controlled cycloaddition. If the reaction of the singlet is accelerated in this manner, it does so at the expense of intersystem crossing to the triplet. When the diylophile substituent is an alkyl group, then the rate of cycloaddition with the singlet is slowed to a point where intersystem crossing to the triplet becomes competitive and bridged cycloadducts, arising from the triplet, are observed (Scheme III).

Scheme III. Reduction of Diyl HOMO–Diylophile LUMO Energy Gap Leads to Rate Acceleration in a Singlet Diyl HOMO-Controlled Reaction[a]



[a] LUMO energies from: Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: New York, 1976; p 128.

Selective Formation of Bridged Cycloadducts by Design. Our major objective in conducting these investigations was to determine how to obtain bridged cycloadducts selectively. To this end, we reasoned that if the substituent, R, was made sufficiently large, then the existence of nonbonded and torsional interactions between it, the tether, the five-membered ring, and the $\cdot CH_2$ unit, would disfavor formation of the linearly fused cycloadduct and favor the sterically less demanding pathway leading to bridged products. Scheme IV illustrates how the 6-*endo,trig* cyclization allows the bulky substituent to assume a position which minimizes nonbonded and torsional interactions, while the alternative 5-*exo,trig* cyclization does not.

The molecular mechanics energy of the diyls formed upon cyclization in both the 5-*exo* and 6-*endo,trig* modes were compared.[11] Calculations were conducted for cases

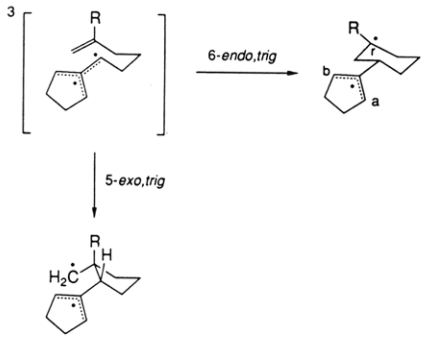
(8) (a) In competition with intramolecular diyl trapping, the singlet is expected to undergo intersystem crossing with $k_{isc} \sim 10^8$–10^9 s^{-1}.[6a] The amount of singlet diyl present at any given time will, therefore, be very low, decreasing the probability of reaction with oxygen. See: Duncan, C. D., Ph.D. Dissertation, Yale University, 1974. (b) Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929. (c) Steel, C.; Clark, W. D. K. *J. Am. Chem. Soc.* **1971**, *93*, 6347. (d) Duncan, C. D.; Corwin, L. R.; Davis, J. H.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2350. The reactions were conducted in a sealed tube at 70 °C for 9 h in the presence of 200 Torr of oxygen; acetonitrile was the solvent.

(9) Goodman, J. L.; Herman, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 2681.

(10) For the reaction of **17-T** with acrylonitrile, E_a = 6.0 kcal mol^{-1} and $A = 10^{8.7}$ M^{-1} s^{-1}. Therefore at 80 °C, $k \sim 10^5$ M^{-1} s^{-1}. Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2358.

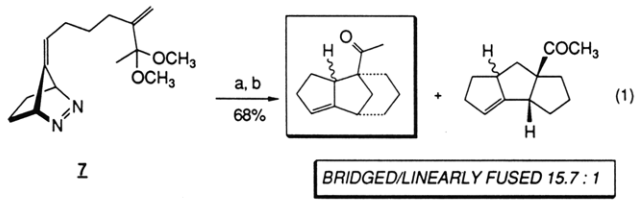
(11) The software required to carry out the molecular mechanics calculations (PC Model) is commercially available from Serena Software, Bloomington, IN. To assure that an energy minimum has been reached, we examined the energy of each structure as a function of rotation about each ring-to-substituent bond. π calculations were *not* included. The results are meant to be used in a *qualitative manner only*. Obviously, they overstate the expected preference for bridged/linearly fused selectivity in the case of R = acetal.

Scheme IV. Comparison of 5-*exo,trig* and 6-*endo,trig* Modes of Cyclization



where R varied from the comparatively small CH_2OH to the more sterically demanding $CH(OMe)_2$ to the large dimethyl ketal $CCH_3(OMe)_2$. It was assumed that a portion of the energy difference between the diyls, that is, a portion of ΔMME, would be reflected in the transition states leading to them, and that the difference would serve as a guide for the selection of the alkyl group most likely to lead to bridged cycloadducts. Table II suggests that as the size of R increases the preference for formation of the bridged cycloadduct ought to increase and reveals that the major contributors to ΔMME are the bending and torsional contributions to the total molecular mechanics energy, MME.

A dimethyl ketal was selected to serve both as a large and a functionalized substituent which could be used in future synthetic manipulations. As shown in Table I, *use of diazene 7 [R = $C(CH_3)(OCH_3)_2$] did indeed provide synthetically useful amounts of the desired bridged cycloadducts (15.7:1 bridged to linear)* (eq 1).

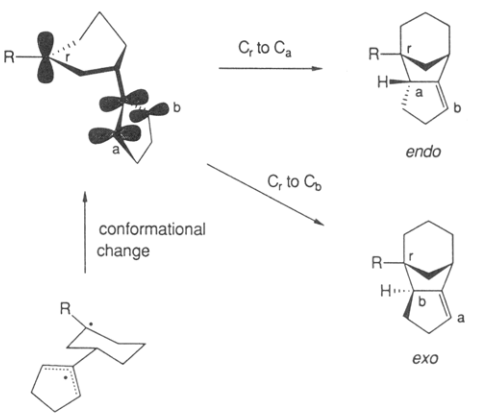


a, THF (1mM), reflux, 3-4 h; b, PPTS, acetone/H_2O, room temp, 0.5 h

Stereochemistry. In the past, we have shown that with only one exception[3a,12] the diyl trapping reaction is a stereoselective process, leading to the preferential formation of cis,anti rather than cis,syn linearly fused tricyclopentanoids.[3b] In those instances, the diylophile was activated by an electron-withdrawing group or it was monorather than disubstituted. The cycloadditions, therefore, probably proceeded via the singlet diyl. The present study shows (note Table I) that regardless of the nature of the substitutent attached to the diylophile, cis,anti stereoselectivity is observed.

Unfortunately, as shown in Table I, bridged cycloadducts are not formed stereoselectively. Scheme V affords some insight into the possible origin of this observation. Focus attention upon the diyl resulting from a 6-*endo,trig* cyclization. In order to form the second σ bond, a conformational change is required to bring the five-membered allylic radical into the vicinity of the second radical site, C_r. Once this is done, then a choice exists between joining C_r to C_a or to C_b of the allylic radical: bonding of C_r to C_a leads to the endo isomer while C_r to

Scheme V. Formation of Endo and Exo Bridged Stereoisomers



C_b affords the exo. Examination of models reveals that there is only a small difference between the movements required to achieve bonding to either site. Furthermore, the group R appears to be too far removed to sterically favor one mode of closure over the other, and low selectivity is predicted and observed.

Concluding Remarks

In summary, *synthetically useful quantities of either bridged or linearly fused cycloadducts can be obtained in the intramolecular diyl trapping reaction.* Bridged cycloadducts arise by intercepting the triplet diyl, while linear products can be produced from either the singlet or the triplet. When an electron-withdrawing group is attached to the diylophile, the singlet diyl leads selectively to linear cycloadducts. On the other hand, the presence of a large alkyl group attached to the internal carbon of the diylophile affords bridged cycloadducts selectively from cycloaddition with the triplet. These discoveries promise to be of utility in a variety of synthetic endeavors. The antitumor agent aphidicolin will serve as a test of the applicability of the methodology to total synthesis.[13]

Experimental Section

Yields refer to isolated materials judged to be homogeneous by TLC and NMR spectroscopy unless specified otherwise. Glassware was oven-dried, and for air-sensitive reactions, solvents and reagents were introduced into the reaction vessel via syringe through a serum cap under an atmosphere of nitrogen. All solvents were distilled and/or dried prior to use, by using standard methods. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen. SSF refers to the light boiling petroleum ether (40–50 °C). The sodium salt of 2-thiopyridine N-oxide was purchased from Pflatz and Bauer. "Dried" refers to drying the organic layer over anhydrous $MgSO_4$ unless otherwise stated. Rochelle's salt refers to a 30% aqueous solution of sodium potassium tartrate. "Base-wash" refers to placing the glassware in an aqueous solution of KOH (ca. 5 M), followed by rinsing with water. Concentration in vacuo refers to initial removal of solvents using a rotary evaporator and subsequent removal of remaining traces on a vacuum pump at ca. 1 Torr.

Thin-layer chromatography (TLC) was performed on silica gel precoated glass plates (E. Merck 60F-254); visualization was accomplished by using an ultraviolet handlamp, or with iodine, *p*-anisaldehyde, $KMnO_4$, and/or phosphomolybdic acid stains. TLC data are reported as follows: solvent mixture (v/v), R_f value,

(12) Loss of diylophile stereochemistry is also rare; only one case has been documented. For a discussion, see: Campopiano, O.; Little, R. D.; Petersen, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3721.

(13) For a recent formal total synthesis of aphidicolin as well as references to previous total and partial syntheses, see: (a) Tanis, S. P.; Chuang, Y.-H.; Head, D. B. *J. Org. Chem.* **1988**, *53*, 4929–4938. (b) Holton, R. A.; Kennedy, R. M.; Kim, H.-B.; Krafft, M. E. *J. Am. Chem. Soc.* **1987**, *109*, 1597–1600.

and the staining agent. Liquid chromatography was carried out on Fluka silica gel 60 (230–400 mesh, ASTM), or ICN Biomedical silica gel (32–63, 60 Å); solvent mixtures were prepared by volume. The chromatography data are presented in the following order: mass of silica gel used, solvent system, and the volume of solvent used. High-performance liquid chromatography (HPLC) was carried out with a refractive index detector and an Altex UltrasilTm-Si (dp 10 f, 10 mm i.d. × 25 cm) or a Cole Scientific Axxiom (silica, 5 μm, 10 mm i.d. × 25 cm) column.

Analytical gas chromatography (GC) was carried out using an Ultra II (Hewlett-Packard, 5% phenyl methyl silicon; 25 m × 0.20 mm) capillary column with helium as the carrier gas unless otherwise stated. Preparative GC was carried out on a 20 ft × 0.25 in. column packed with 5% SE 30 on Chromosorb W.

6-(*tert*-Butyldimethylsiloxy)-2-methylidenehexan-1-ol. To 131 mL of *n*-butyllithium cooled to −78 °C was added *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, 24.3 g, 209 mmol, freshly distilled from CaH_2) via syringe over 5 min. Upon addition of TMEDA a white precipitate formed. After 10 min, methallyl alcohol (7.54 g, 104.6 mmol) was added dropwise via syringe (5 min), and the resulting heterogeneous mixture was stirred for 17 h as the yellow suspension warmed from −78 to 24 °C. The mixture was recooled to −78 °C and 3-bromo-1-(*tert*-butyldimethylsiloxy)propane (11.03 g, 43.55 mmol) in THF (22 mL, 2 M) was added dropwise via syringe (5 min). After 10 min, the reaction was quenched with 100 mL of 0.5 N HCl, the layers were separated, the aqueous layer was extracted with Et_2O (5 × 50 mL), and the combined organic layers were washed with brine (150 mL), dried, and concentrated in vacuo to afford 10.94 g of crude product. Chromatography on silica gel (600 g; 10% Et_2O/SSF, 3000 mL; 20% Et_2O/SSF, 2000 mL; 30% Et_2O/SSF, 1000 mL) afforded 8.32 g of alcohol (78%). TLC (20% Et_2O/SSF): R_f 0.18, I_2, *p*-anis. FTIR (neat, NaCl): 3466–3206, 3090, 2943, 2859, 1656, 1484, 1465, 1269, 1105, 1040, 779 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.03 (br s, 1 H, vinyl), 4.88 (apparent t, 1 H, *J* = 1, vinyl), 4.08 (d, 2 H, *J* = 6.5, $CH_2C[=CH_2]CH_2OH$), 3.62 (t, 2 H, *J* = 6, R_3SiOCH_2), 2.07 (t, 2 H, *J* = 7.5, $CH_2C[=CH_2]CH_2OH$), 1.53 (m, 4 H, CH_2CH_2), 1.38 (apparent t, 1 H, *J* = 6, OH), 0.89 (s, 9 H, $[CH_3]_3CSiO$), 0.048 (s, 6 H, CH_3SiO). LRMS (CI, CH_4): *m/z* (rel int) 131 ($M^+ - C_6H_{13}Si$, 10), 113 (15), 95 (100), 75 (30), 67 (20), 57 (10), 43 (20). Anal. Calcd for $C_{13}H_{28}O_2Si$: C, 63.93; H, 11.48. Found: C, 63.89; H, 11.39.

1-(Benzoyloxy)-2-methylidene-6-(*tert*-butyldimethylsiloxy)hexane. To a mixture of alcohol (0.737 g, 3.01 mmol), pyridine (1.19 g, 15.1 mmol), and 4-(dimethylamino)pyridine (0.073 g, 0.6 mmol) in CH_2Cl_2 (6 mL, 0.5 M) at 0 °C was added benzoyl chloride (0.847 g, 6.0 mmol) dropwise, via syringe, over 5 min. The cold bath was removed, and the reaction mixture was allowed to reach room temperature. After 1 h, water (10 mL) was added and the resulting heterogeneous mixture was stirred for an additional 0.5 h. The layers were separated, the aqueous layer was extracted with Et_2O (5 × 15 mL), and the organic layers were combined, washed with saturated aqueous $CuSO_4$ (2 × 15 mL) and brine (30 mL), dried, and concentrated in vacuo to afford 1.72 g of crude product. Upon chromatography on silica gel (50 g; 10% Et_2O/SSF, 500 mL) 1.01 g of benzoate was obtained (96%). TLC (20% Et_2O/SSF): R_f 0.8, UV, I_2, *p*-anis. FTIR (neat, NaCl): 3083, 2931, 2858, 1723, 1656, 1614, 1471, 1393, 1269, 1182, 1110, 1070, 1027, 837, 776, 709 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.06 (apparent d, 2 H, *J* = 7, ortho H), 7.57 (apparent t, 1 H, *J* = 7, para H), 7.45 (t, 2 H, *J* = 7.5, meta H), 5.13 (s, 1 H, vinyl), 5.00 (s, 1 H, vinyl), 4.78 (s, 2 H, $CH_2C[=CH_2]CH_2OBz$), 3.63 (t, 2 H, *J* = 6, R_3SiOCH_2), 2.17 (apparent t, 2 H, *J* = 6.5, $CH_2C[=CH_2]CH_2OBz$), 1.56 (m, 4 H, CH_2CH_2), 0.89 (s, 9 H, $[CH_3]_3CSiO$), 0.043 (s, 6 H, CH_3SiO). LRMS (CI, CH_4): *m/z* (rel int) 349 (M^+ + 1, 4), 227 (21), 221 (15), 180 (14), 179 (100), 105 (26), 95 (36), 75 (6), 47 (5). Anal. Calcd for $C_{20}H_{32}O_3Si$: C, 68.97; H, 9.20. Found: C, 68.97; H, 9.45.

1-(Benzoyloxy)-2-methylidenehexan-6-ol. To a solution of benzoate (1.01 g, 2.89 mmol) in CH_3CN (4 mL, 0.77 M) was added HF/CH_3CN (3.2 M HF, 1:9 v/v, 1 mL), and the resulting mixture was stirred for 2.5 h at room temperature. Brine (10 mL) was added, the aqueous layer was extracted Et_2O (5 × 25 mL), and the organic layers were combined, washed with brine (30 mL), dried, and concentrated in vacuo to afford 0.742 g of crude product. Upon chromatography on silica gel (30 g; 60% Et_2O/SSF, 500 mL) 0.652 g of alcohol was obtained (96%). TLC (60% Et_2O/SSF): R_f 0.27, UV, *p*-anis. FTIR (neat, NaCl): 3597–3118, 3085, 2936, 2871, 1717, 1662, 1452, 1272, 1113, 711 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, 2 H, *J* = 7, ortho H), 7.57 (t, 1 H, *J* = 7.5, para H), 7.45 (t, 2 H, *J* = 7.5, meta H), 5.15 (s, 1 H, vinyl), 5.01 (s, 1 H, vinyl), 4.79 (s, 2 H, $CH_2C[=CH_2]CH_2OBz$), 3.76 (apparent d, 2 H, *J* = 5, CH_2OH), 2.19 (t, 2 H, *J* = 7, $CH_2C[=CH_2]CH_2OBz$), 1.07 (m, 4 H, *CH*), 1.29 (t, 1 H, *J* = 5, OH). LRMS (CI, CH_4): *m/z* (rel int) 235 (M^+ + 1, 3), 123 (10), 113 (10), 105 (30), 95 (20), 75 (77), 59 (65), 47 (100). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.53; H, 7.84.

1-(Benzoyloxy)-2-methylidenehexan-6-al. To a slurry of alcohol (0.628 g, 2.67 mmol) and Celite (3 g) in CH_2Cl_2 (26 mL, 0.1 M) was added pyridinium chlorochromate (PCC, 1.74 g, 8.03 mmol) at room temperature. After 2 h, Et_2O (30 mL) was added to precipitate the chromium residues. Filtration through Florisil and concentration in vacuo afforded 0.595 g of crude product. Upon chromatography on silica gel (30% Et_2O/SSF, 500 mL), 0.551 g aldehyde was obtained (85%). TLC (30% Et_2O/SSF): R_f 0.22, UV, *p*-anis. FTIR (neat, NaCl): 3080, 2938, 2827, 2725, 1731, 1720, 1655, 1602, 1451, 1388, 1314, 1266, 1186, 1111, 1071, 1032, 912, 712 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.79 (t, 1 H, *J* = 1.8, *CHO*), 8.05 (apparent d, 2 H, *J* = 6.9, ortho H), 7.55 (apparent t, 1 H, *J* = 7.5, para H), 7.45 (t, 2 H, *J* = 7.8, meta H), 5.18 (s, 1 H, vinyl), 5.02 (s, 1 H, vinyl), 4.78 (s, 2 H, $C[=CH_2]CH_2OBz$), 2.50 (td, 2 H, *J* = 13, 1.0, $OCHCH_2CH_2$), 2.20 (t, 2 H, *J* = 7.5, $CH_2C[=CH_2]CH_2OBz$), 1.87 (quintet, 2 H, *J* = 7.5, $CH_2CH_2CH_2$). LRMS (CI, CH_4): *m/z* (rel int) 233 (M^+ + 1, 6.5), 215 (28), 123 (12.8), 111 (82.6), 105 (100), 93 (17.9), 75 (13.6). Exact mass [HRMS (CI)] calcd for $C_{14}H_{17}O_3$ (M^+ + 1) 233.1178, found 233.1178.

6-(4-((Benzoyloxy)methyl)-4-pentenyl)fulvene. To a solution of aldehyde (0.55 g, 2.37 mmol) and cyclopentadiene (0.39 g, 5.93 mmol) in MeOH (5 mL, 0.47 M) at 0 °C was added Et_2NH (0.26 g, 3.56 mmol) dropwise via syringe over 5 min. The resulting homogeneous mixture was stirred at room temperature and was monitored by TLC. After 2.5 h, the reaction mixture was cooled to 0 °C, and glacial HOAc (0.28 g, 4.74 mmol) was added in one portion. The solution was diluted with H_2O (10 mL) and Et_2O (10 mL), the aqueous layer was extracted with Et_2O (5 × 30 mL), and the organic layers were combined, washed with brine (30 mL), dried, and concentrated in vacuo to afford 0.45 g of crude fulvene. Chromatography on silica gel (50 g; 5% Et_2O/SSF, 500 mL) afforded 0.603 g of fulvene as a bright yellow oil (91%). TLC (10% Et_2O/SSF): R_f 0.52, UV, *p*-anis. FTIR (neat, NaCl): 3074, 2938, 2873, 1721, 1653, 1607, 1456, 1270, 1181, 1112, 1032, 909, 766, 712, 617 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.04 (apparent dd, 2 H, *J* = 8.4, 0.9, ortho H), 7.59 (t, 1 H, *J* = 7.5, para H), 7.44 (apparent t, 2 H, *J* = 6.9, meta H), 6.51 (m, 4 H, Cp vinyl H), 6.18 (dt, 1 H, *J* = 3, 5.1, exocyclic vinyl H), 5.19 (s, 1 H, vinyl), 5.02 (s, 1 H, vinyl), 2.59 (q, 2 H, *J* = 7.5, allylic H next to exocyclic double bond), 2.13 (t, 2 H, *J* = 7.8, $CH_2CH_2C[=CH_2]CH_2OBz$), 1.77 (quintet, 2 H, *J* = 7.5, $CH_2CH_2CH_2$). LRMS (CI, CH_4): *m/z* (rel int) 280.1 (1.9, M^+, no M^+ + 1 was seen), 159 (54.8), 158 (27.9), 131 (19), 123 (10.6), 117 (22), 105 (100), 91 (18.4), 79 (35.5), 75 (13.2), 67 (13.6). exact mass [HRMS (CI)] calcd for $C_{19}H_{20}O_2$ (M^+) 280.1463, found 280.1464.

Dimethyl 2,3-Diaza-7-(5′-((benzoyloxy)methyl)hex-5′-enylidene)bicyclo[2.2.1]heptane-2,3-dicarboxylate. To a solution of fulvene (1.25 g, 4.45 mmol) in CH_2Cl_2 (17 mL, 0.25 M) at room temperature was added dimethyl azodicarboxylate (0.65 g, 4.45 mmol) in CH_2Cl_2 (3 mL). The resulting mixture was placed in the refrigerator overnight (8 h). The solvent was removed in vacuo (foaming) to afford 2.4 g of crude carbamate, which was reduced without further purification. TLC (100% Et_2O): R_f 0.37, UV, *p*-anis. FTIR (neat, NaCl, crude): 3045, 2959, 2862, 1784, 1717, 1444, 1314, 1272, 1247, 1188, 1109, 713 cm^{-1}. ^1H NMR (crude, 500 MHz, $CDCl_3$): δ 8.05 (apparent dd, 2 H, *J* = 18, 1, ortho H), 7.58 (t, 1 H, *J* = 8.5, para H), 7.46 (apparent t, 2 H, *J* = 8, meta H), 6.67 (br s, 2 H, endocyclic vinyls) 5.13 (s, vinyl), 4.97 (s, vinyl), 4.91 (t, *J* = 8, exocyclic vinyl), 4.75 (s, $CH_2C[CH_2]CH_2OBz$), 5.13–4.75 ppm integrates for 7 H which include the bridgehead H, 3.76 (s, 6 H, OCH_3), 2.06 (m, 4 H, allylic H), 1.55 (quintet, 2 H, *J* = 7.5, $CH_2CH_2CH_2$).

To a heterogeneous mixture of the crude carbamate (2.4 g, 5.6 mmol) and dipotassium azodicarboxylate (5.46 g, 28.1 mmol) in

dry CH_2Cl_2 (23 mL, 0.25 M) at 0 °C was added glacial HOAc (3.38 g, 56.3 mmol) in CH_2Cl_2 (19 mL, 3 M) dropwise via syringe over 15 min (gas evolution noted). After 1.5 h, the reaction mixture was filtered, the filter cake was washed with CH_2Cl_2, the solution was concentrated in vacuo, and the residue was chromatographed on silica gel (50 g; 50% Et_2O/SSF) to afford 1.8 g of pure reduced carbamate (94% over two steps). TLC (100% Et_2O): R_f 0.68, UV, *p*-anis. FTIR (neat, NaCl): 3067, 2940, 2861, 1750, 1704, 1653, 1601, 1442, 1272, 1114, 1070, 1027, 926, 769, 715 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.05 (apparent d, 2 H, J = 6.9, ortho H), 7.57 (apparent t, 1 H, J = 7.5, para H), 7.45 (t, 2 H, J = 7.8, meta H), 5.36 (t, 1 H, J = 7.2, exocyclic vinyl), 5.14 (s, 1 H, vinyl), 4.99 (s, 1 H, vinyl), 4.77 (s, $CH_2C[=CH_2]CH_2OBz$), 4.99–4.77 (5 H, 1 vinyl H, $CH_2C[=CH_2]CH_2OBz$ H, and 2 bridgehead H), 3.78 (s, 6 H, OCH_3), 2.1 (t, J = 6, allylics), 1.85 (broad s), 1.59 (quintet, J = 7.8, $CH_2CH_2CH_2$), 3.78 to 1.59 (10 H, 4 allylics H, 4 endo/exo H, 2-CH_2). LRMS (EI): m/z (rel int) 428 (M^+, 4), 279 (11), 159 (23), 158 (23), 117 (11), 106 (10), 105 (100), 93 (12), 91 (17), 77 (36), 59 (17), 44 (10). Anal. Calcd for $C_{23}H_{28}O_6N_2$: C, 64.47; H, 6.58. Found: C, 64.26; H, 6.74.

2,3-Diaza-7-(5′-(hydroxymethyl)hex-5′-enylidene)bicyclo[2.2.1]hept-2-ene (5). To a solution of reduced carbamate (0.793 g, 1.85 mmol) in EtOH (17 mL, 0.11 M) was added KOH (1.87 g, 33.3 mmol). The resulting solution was refluxed for 1.5 h, the reaction mixture was cooled to 0 °C, and $K_3Fe(CN)_6$ (1.83 g, 5.6 mmol) in H_2O (15 mL, 0.38 M) was added via syringe over 10 min. After 1 h, brine (20 mL) was added, the aqueous layer was extracted with 10% THF/Et_2O (5 × 40 mL), and the organic layers were combined, washed with brine (50 mL), dried, and concentrated in vacuo to afford 0.40 g of crude diazene. Upon chromatography on silica gel (10 g, 100% Et_2O, 300 mL), 0.370 g of diazene **5** was obtained (97%). TLC (100% Et_2O): R_f 0.4, I_2, *p*-anis. FTIR (neat, NaCl) 3632–3125, 2963, 2865, 1655, 1482, 1446, 1043, 906 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 5.35 (d, 1 H, J = 2.5, bridgehead H), 5.08 (overlapping t and d, 2 H, J = 7, 3.5, exocyclic vinyl H, bridgehead H), 5.01 (s with fine coupling, 1 H, J = 0.5, vinyl), 4.82 (s with fine coupling, 1 H, J = 1, vinyl), 4.05 (s, 2 H, $CH_2C[=CH_2]CH_2OH$), 1.99 (m, 4 H, allylic H), 1.61 (m, 2 H, exo H), 1.47 (quintet, 2 H, J = 7.5, $CH_2CH_2CH_2$), 1.08 (apparent d, 2 H, J = 7.5, endo H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148 (vinyl), 117 (vinyl), 109.9 (vinyl), 77.1 (C_1), 72.8 (C_4), 66 (C_7), 32.4, 28.8, 27.7, 21.8, 21.3. LRMS (CI, CH_4): m/z (rel int) 207 (M^+ + 1, 100), 189 (60), 179 (40), 161 (100), 147 (30), 131 (30), 119 (30), 105 (30), 91 (50), 79 (50), 67 (70). Exact mass [HRMS (CI)] calcd for $C_{12}H_{19}ON_2$ (M^+ + 1) 207.1497, found 207.1497.

Diyl Trapping Reaction: Diazene 5. A solution of diazene **5** (0.014 g, 0.07 mmol) in CH_3CN (47 mL, 1.5 mM) was degassed by bubbling Ar through the solution for 30 min. The solution was then refluxed for 4 h (Ar) and cooled to room temperature, the solvent was removed in vacuo, and the product mixture was analyzed by capillary column GC. The crude mixture was purified on silica gel (20% Et_2O/SSF) to afford 11 mg of trapped products (90%). The ratio of cis,anti:cis,syn:exo:endo bridged cycloadducts was 12.04:1.0:7.9:9.1 and that of linear to bridged was 1.0:1.2. The trapped products were separated by HPLC (Altex Ultrasil column) using 10% EtOAc/hexane (flow rate; 2 mL/min) as the eluting solvent. The pertinent spectral data are reported below.

(3aβ,6aα,7aβ)-2,3,3a,5,6,6a,7,7a-Octahydro-1*H*-cyclopenta[*a*]pentalene-7a-methanol. TLC (10% Et_2O/SSF): R_f 0.12, I_2, *p*-anis. FTIR (neat, NaCl): 3648–3085, 3053, 2932, 2858, 1448, 1031 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.22 (s, 1 H, vinyl), 3.48 (d, 1 H, J = 10.5, CH_2OH), 3.43 (d, 1 H, J = 10.5, CH_2OH), 3.10 (m, 1 H, H on C_{6a}), 2.54 (m, 3 H, allylic bridgehead H on C_{3a} and allylic H on C_5), 2.10 (dt, 1 H, J = 12.5, 12.5, 1 Hz, H on C_6), 1.9 (m, 1 H, H on C_3), 1.76 (m, 2 H, 1 H on C_7), 1.65 (m, 2 H), 1.5 (m, 2 H), 1.38 (m, 2 H, 1 H on C_6), 1.10 (apparent t, 1 H, J = 10.5 Hz, H on C_7). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.07 (C_{4a}), 117.42 (C_4), 70.21 (CH_2OH), 60.97 (C_{6a}), 49.49 (C_{3a}), 44.41 (C_1), 42.94 (C_{7a}), 37.26 (C_5), 37.15, 34.48, 32.06, 27.12 (C_6). LRMS (EI): m/z (rel int) 178 (M^+, 21), 160 (21), 147 (30), 131 (50), 117 (80), 105 (40), 91 (98), 79 (100), 67 (65), 53 (20), 43 (10). Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.96; H, 10.28.

(3aα,4α,8α)-2,3,3a,4,5,6,7,8-Octahydro-4,8-methanoazulene-4-methanol (12). TLC (20% Et_2O/SSF): R_f 0.2, I_2, *p*-anis. FTIR (neat, NaCl): 3437–3084, 3054, 2932, 2873, 1459, 1030, 809 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.5 (s, 1 H, vinyl), 3.55 (d, 1 H, J = 10.5, CH_2OH), 3.46 (d, 1 H, J = 10.5, CH_2OH), 2.69 (apparent t, 1 H, J = 3.5, allylic bridgehead H on C_8), 2.61 (m, 1 H, allylic bridgehead H on C_{3a}), 2.44 (m, 1 H, allylic H on C_2), 2.21 (m, 1 H, allylic H on C_2), 1.98 (m, 1 H, H on C_3), 1.65 (m), 1.48 (m), 1.31 (m), 1.65–1.48 (10 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.09 (C_{8a}), 120.79 (C_1), 68.64 (CH_2OH, C_{10}), 52.91 (C_{3a}), 43.23 (C_8), 38.31 (C_2), 35.66 (C_3), 33.98, 33.03, 29.77 (C_7), 19.56 (C_6). LRMS (EI): m/z (rel int) 178 (M^+, 30), 160 (20), 147 (10), 131 (25), 117 (45), 105 (20), 91 (90), 79 (100), 67 (60), 63 (5), 53 (20), 43 (5). Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.86; H, 10.13.

(3aβ,4α,8α)-2,3,3a,4,5,6,7,8-Octahydro-4,8-methanoazulene-4-methanol (13). TLC (20% Et_2O/SSF): R_f 0.2, I_2, *p*-anis. FTIR (neat, NaCl): 3558–3072, 3048, 2932, 2862, 1471, 1037, 798 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 5.20 (s, 1 H, vinyl), 3.43 (s, 2 H, CH_2OH), 2.75 (m, 3 H, allylic bridgeheads on C_{3a}, C_8, allylic H on C_2), 2.54 (m, 1 H, allylic H on C2), 1.9–1.4 (m, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 115.85 (C_1), 71.54 (CH_2OH), 59.07 (C_{3a}), 46.62 (C_8), 37.34 (C_2), 34.15 (C_4), 33.86 (C_9), 29.62, 28.93, 26.03, 18.42 (C_6). LRMS (EI): m/z (rel int) 178 (M^+, 35), 160 (25), 147 (30), 131 (40), 117 (50), 105 (40), 91 (90), 79 (100), 67 (60), 63 (5), 53 (20), 43 (10). Exact mass [HRMS (EI)] calcd for $C_{12}H_{18}O$ (M^+) 178.1358, found 178.1357.

(3aβ,6aβ,7aβ)-2,3,3a,5,6,6a,7,7a-Octahydro-1*H*-cyclopenta[*a*]pentalene-7a-methanol. TLC (20% Et_2O/SSF): R_f 0.2, I_2, *p*-anis. FTIR (neat, NaCl): 3421–3137, 2930, 2858, 1471, 1037 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.21 (s, 1 H, vinyl), 3.3 (s, 2 H, CH_2OH), 2.6 (m), 2.4 (m), 2.1 (m), 2.6–2.1 (3 H), 1.6 (m), 1.2 (m), 1.6–1.2 (12 H). LRMS (EI): m/z (rel int) 178 (M^+, 10), 147 (70), 119 (60), 91 (100), 67 (70). Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 81.02; H, 10.34.

2,3-Diaza-7-[5′-formyl-5′-methylidenepentanylidene]bicyclo[2.2.1]hept-2-ene. To a suspension of Dess–Martin periodinane (0.16 g, 0.38 mmol) in CH_2Cl_2 (1.5 mL, 0.28 M) at room temperature was added diazene **5** (0.071 g, 0.34 mmol) in CH_2Cl_2 (1.2 mL, 0.28 M) over 3 min. Upon addition, the suspension turned a milky color. After 5 min, the mixture was diluted with 50% Et_2O/SSF (5 mL), filtered through silica gel, and concentrated in vacuo. Purification on silica gel (0.5 g, 50% Et_2O/SSF, 200 mL) afforded 68 mg of pure aldehyde (97%). TLC (50% Et_2O/SSF): R_f 0.24, I_2, *p*-anis. IR (neat, NaCl) 3010, 2950, 2870, 2830, 1685 (br), 1480, 1150, 1050, 1040, 870 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 9.53 (s, 1 H, CHO), 6.23 (s, 1 H, vinyl), 6.01 (s, 1 H, vinyl), 5.37 (s, 1 H, bridgehead H), 5.20 (m, 2 H, bridgehead H, vinyl), 2.19 (t, 2 H, J = 7.5, allylic H), 2.00 (m, 2 H, endo H), 1.49 (quintet, 2 H, J = 8, $CH_2CH_2CH_2$), 1.23 (apparent d, 2 H, J = 10, exo H). LRMS (CI, CH_4): m/z (rel int) 205 (M^+ + 1, 8), 177 (33), 175 (25), 159 (100), 149 (11), 133 (44), 91 (14), 67 (15). Exact mass [HRMS, (CI)] calcd for $C_{12}H_{17}ON_2$ (M^+ + 1) 205.1341, found 205.1341.

2,3-Diaza-7-(5′-methylidene-6′-hydroxyheptanylidene)bicyclo[2.2.1]hept-2-ene. To a solution of diazene aldehyde (0.046 g, 0.23 mmol) in Et_2O (3 mL, 0.075 M) at −78 °C was added methyllithium (0.23 mL, 0.33 mmol) dropwise over 3 min. After 45 min, the reaction was quenched with saturated aqueous ammonium chloride (2 mL). Upon warming to room temperature, the layers were separated, the aqueous layer was extracted with Et_2O (5 × 10 mL), and the combined organic layers were washed with brine (10 mL), dried, and concentrated in vacuo. Chromatography on silica gel (1 g, 70% Et_2O/SSF, 200 mL) afforded 37 mg of pure alcohol (74%). TLC (70% Et_2O/SSF): R_f 0.22, I_2, *p*-anis. IR (neat, NaCl): 3700–3100, 2950, 2850, 1640, 1450, 1100, 900 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.38 (s, 1 H, bridgehead H), 5.12 (overlapping t, s, 2 H, exocyclic vinyl, J = 7.8, bridgehead H), 5.05 (s, 1 H, vinyl), 4.78 (s, 1 H, vinyl), 4.24 (apparent br d, 1 H, J = 5.7, $CHOH$), 2.01 (m, 4 H, allylic H), 1.63 (m, 2 H, endo H), 1.51 (quintet, 2 H, J = 7.5, $CH_2CH_2CH_2$), 1.26 (d, 3 H, J = 6.9, CH_3), 1.09 (apparent d, 2 H, J = 8.7, exo H). LRMS (CI, CH_4): m/z (rel int) 221 (M^+ + 1, 3), 203 (12), 191 (14), 175 (100), 159 (5), 147 (13), 119 (11), 95 (12), 67 (7). Exact mass [HRMS (CI)] calcd for $C_{13}H_{21}ON_2$ (M^+ + 1) 221.1654, found 221.1654.

2,3-Diaza-7-(5′-methylidene-6′-oxoheptanylidene)bicyclo[2.2.1]hept-2-ene (4). To a suspension of Dess–Martin periodinane (0.356 g, 0.84 mmol) in CH_2Cl_2 (3.4 mL, 0.25 M) at room

temperature was added diazene alcohol (0.15 g, 0.70 mmol) via syringe over 3 min. After 20 min, the mixture was diluted with 50% Et_2O/SSF (10 mL), filtered over silica gel, and concentrated in vacuo. Chromatography on silica gel (2 g, 50% Et_2O/SSF, 250 mL) afforded 152 mg of unsaturated ketone (100%). TLC (50% Et_2O/SSF): R_f 0.22, I_2, *p*-anis. IR (neat, NaCl) 3010, 2950, 1680, 1450, 1360, 1250, 940 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.95 (s, 1 H, vinyl), 5.68 (s, 1 H, vinyl), 5.3 (s with fine coupling, 1 H, J = 1.8, bridgehead H), 5.04 (t, 2 H, J = 7.8, vinyl and bridgehead H), 2.26 (s, 3 H, CH_3), 2.13 (t, 2 H, J = 6.9, allylic H), 1.91 (m, 2 H, allylic H), 1.59 (d with fine coupling, 2 H, J = 9.9, 1.8, endo H), 1.37 (quintet, 2 H, J = 6.9, $CH_2CH_2CH_2$), 1.05 (d with fine coupling, 2 H, J = 8.4, 2.4, exo H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5 ($C_{6'}$), 148 (C_7), 144.8 ($C_{5'}$), 125 ($C_{8'}$), 116.8 ($C_{1'}$), 76.6 (C_1 or C_4), 72.4 (C_1 or C_4), 29.8 (CH_3), 28.5 (allylic), 28.03 (allylic), 25.69 ($C_{3'}$), 21.3 (C_5 or C_6), 20.87 (C_5 or C_6). LRMS (CI, CH_4): m/z (rel int) 219 (M^+ + 1, 23), 191 (88), 173 (100), 133 (54), 119 (61), 109 (7), 105 (7), 91 (10), 69 (10). Exact mass [HRMS (CI)] calcd for $C_{13}H_{19}ON_2$ (M^+ + 1) 219.1497, found 219.1498.

2,3-Diaza-7-(6′,6′-dimethoxy-5′-methylideneheptanylidene)bicyclo[2.2.1]hept-2-ene (7). To a mixture of diazene ketone **4** (0.071 g, 0.028 mmol) and trimethyl orthoformate (0.26 mL, 2.3 mmol) in methanol (1 mL, 0.78 M) at room temperature was added pyridinium *p*-toluenesulfonate (2 mg, 0.008 mmol). The reaction mixture was stirred at 4 °C for 24 h, K_2CO_3 (10 mg) was added, and the mixture was filtered into a freshly based-washed and flame-dried flask (traces of water and acid causes the ketal to revert back to the ketone). Upon concentration in vacuo and preparative TLC (50% Et_2O/SSF), 5 mg of diazene ketal **7** was obtained (83% based on recovered starting material). TLC (50% Et_2O/SSF): R_f 0.42, *p*-anis. IR (neat, NaCl) 3010, 2940, 2850, 1460, 1375, 1150, 1050, 850 cm^{-1}. ^1H NMR (500 MHz, C_6D_6) δ 5.59 (s, 1 H, bridgehead H), 5.2 (s with fine coupling, 1 h, J = 2.5, vinyl), 5.0 (m, 1 H, bridgehead), 4.8 (s with fine coupling, 1 H, J = 2.5, vinyl), 4.73 (t, 1 H, J = 7.5, vinyl), 3.04 (s, 6 H, OCH_3), 1.94 (t, 2 H, J = 7.5, allylic H), 1.71 (m, 2 H, allylic H), 1.36 (m, 2 H, endo H), 1.14 (m, 2 H, $CH_2CH_2CH_2$), 0.84 (d, 2 H, J = 7.5, exo H). Since the diazene was thermally labile, no MS or combustion analysis was obtained.

Diyl Trapping Reaction: Ketal 7 in THF. Diazene ketal **7** (0.037 g, 0.14 mmol) was dissolved in dry THF (170 mL, 0.82 mM, base-washed flask). The mixture was degassed with argon for 45 min and refluxed for 3.5 h. Upon cooling to room temperature, and concentration in vacuo, the crude NMR (C_6D_6) indicated the presence of three products. Due to the instability of the ketals toward chromatography, they were hydrolyzed to afford the corresponding ketones. Thus, the crude reaction mixture was dissolved in acetone (1 mL), and a drop of water and 2 mg of pyridinium *p*-toluenesulfonate were added. After 0.5 h, the mixture was diluted with saturated $CuSO_4$ (1 mL) and Et_2O (3 mL). The layers were separated, the aqueous layer was extracted with Et_2O (3 × 5 mL), and the combined organic layers were washed with brine (5 mL), dried, and concentrated in vacuo. Chromatography on silica gel (0.5 g, 5% Et_2O/SSF) afforded 18 mg (68% over two steps) of a mixture of three products in a ratio of 1:8.2:7.5 (CA:Exo:Endo). The ratio of linear to bridged products was 1.0:15.7. The isomers were separated by HPLC (Axxiom column) using 1% Et_2O/hexane (flow rate: 3 mL/min) as the eluting solvent. Pertinent spectral data are reported below.

((3aβ,6aα,7aβ)-2,3,3a,5,6,6a,7,7a-Octahydro-1*H*-cyclopenta[*a*]pentalen-7a-yl)-1-ethanone. TLC (5% Et_2O/SSF): R_f 0.24, I_2, *p*-anis. IR (neat, NaCl): 3010, 2940, 2860, 1702, 1450, 1360, 1150, 800 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.29 (s, 1 H, vinyl), 3.17 (m, 2 H, allylic bridgehead H on C_{3a} and C_{6a}), 2.56 (m, 2 H, allylic H on C_5), 2.18 (m, 2 H, H on C_6 and H on C_7), 2.10 (s, 3 H, CH_3), 1.95 (m, 2 H, H on C_1), 1.70–1.40 (m, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.1 (C_8), 160.0 (C_4), 118.4 (C_{4a}), 71.9 (C_{7a}), 49.70 (C_{3a}), 44.0 (C_{6a}), 43.2 (C_5), 37.6 (CH_2), 37.4 (CH_2), 34.7 (CH_2), 31.9 (CH_2), 25.8 (C_9), 21.4 (CH_2). LRMS (CI, CH_4): m/z (rel int) 191 (M^+ + 1, 48), 173 (100), 147 (30), 133 (80), 121 (20), 109 (20), 95 (20), 81 (20), 69 (60). Exact mass [HRMS (CI)] calcd for $C_{13}H_{19}O$ (M^+ + 1) 191.1436, found 191.1436.

((3aα,4aα,8aα)-2,3,3a,4,5,6,7,8-Octahydro-4,8-methanoazulen-4-yl)-1-ethanone. TLC (5% Et_2O/SSF): R_f 0.18, I_2, *p*-anis. IR (neat, NaCl): 3010, 2960, 2860, 1705, 1360, 1230, 1050, 800 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.56 (br s with fine coupling, 1 H, J = 1.5, vinyl), 2.9 (br s, 1 H, allylic bridgehead H on C_{3a}), 2.71 (br s, 1 H, allylic bridgehead H on C_8), 2.40 (m, 1 H, allylic H on C_2), 2.19 (apparent ddd, 1 H, J = 3.5, allylic H on C_2), 2.11 (s, 3 H, CH_3), 2.03 (quintet, 1 H, J = 6, H on C_3), 1.91 (m, 1 H, endo H on C_9), 1.8–1.45 (m, 7 H), 1.42 (d, 1 H, J = 11.5, exo H on C_9), 1.3 (m, 1 H, H on C_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.3 (C_{10}), 155.7 (C_{8a}), 122.2 (C_1), 55.2 (C_8), 53.4 (C_{3a}), 41.3 (C_2), 38 (C_{11}), 35.8 (C_3), 33.8 (C_5, C_9), 29.0 (C_7), 19.5 (C_6). LRMS (CI, CH_4): m/z (rel int) 191 (M^+ + 1, 100), 173 (60), 161 (10), 147 (35), 133 (40), 123 (35), 117 (15), 109 (38), 95 (30), 91 (30), 81 (32), 67 (65). Exact mass [HRMS (CI)] calcd for $C_{13}H_{19}O$ (M^+ + 1) 191.1436, found 191.1436.

((3aβ,4aα,8aα)-2,3,3a,4,5,6,7,8-Octahydro-4,8-methanoazulen-4-yl)-1-ethanone. TLC (5% Et_2O/SSF): R_f 0.20, I_2, *p*-anis. IR (neat, NaCl): 3010, 2950, 2860, 1705, 1450, 1350, 1150, 800 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.24 (br s with fine coupling, 1 H, J = 1.5, vinyl), 3.06 (m, 1 H, bridgehead H on C_{3a}), 2.80 (br s, 1 H, bridgehead H on C_8), 2.73 (m, 1 H, allylic H on C_2), 2.60 (m, 1 H, allylic H on C_2), 2.29 (apparent dd, 1 H, J = 5.5, endo H on C_9), 2.11 (s, 3 H, CH_3), 1.88 (m, 3 H), 1.71 (d, 1 H, J = 11.5, exo H on C_9), 1.5 (m, 5 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.4 (C_{10}), 155.7 (C_{8a}), 117.0 (C_1), 58.9 (C_{3a}), 46.4 (C_4), 46.3 (C_8), 37.2 (C_2), 33.4 (C_9), 33.3 (C_{11}), 29.7 (CH_2), 28.4 (CH_2), 26.5 (CH_2), 18.6 (C_6). LRMS (CI, CH_4): m/z (rel int) 191 (M^+ + 1, 100), 173 (60), 161 (15), 147 (40), 133 (40), 123 (40), 109 (45), 95 (50), 91 (35), 81 (55), 69 (100), 65 (10). Exact mass [HRMS (CI)] calcd for $C_{13}H_{19}O$ (M^+ + 1) 191.1436, found 191.1436.

Diyl Trapping Reaction: Diazene 4 in THF. A solution of diazene ketone **4** (0.020 g, 0.091 mmol) in THF (76 mL, 1.2 mM) was degassed with argon for 45 min and refluxed for 3 h. Upon cooling the mixture to room temperature, concentration, and chromatography on silica gel (0.5 g, 10% Et_2O/SSF, 200 mL) 17 mg of pure products was obtained (98%). The mixture contained cis,anti (CA) and cis,syn (CS) linearly fused tricyclopentanoid as well as endo and exo bridged products in a ratio of 36.4:1.0:3.3:1.9 (CA:CS:exo:endo) by capillary column GC. The ratio of linear to bridge products was 7.3:1.0. The spectral data for CA, exo, and endo isomers were reported earlier.

2,3-Diaza-7-(6′,6′-dimethoxy-5′-methylidenehexanylidene)bicyclo[2.2.1]hept-2-ene (6). To a solution of diazene aldehyde (0.065 g, 0.32 mmol) in methanol (2 mL, 0.16 M) was added trimethylorthoformate (1.0 mL, 9.5 mmol) and pyridinium *p*-toluenesulfonate (0.016 g, 0.06 mmol). The resulting solution was stirred at 4 °C for 4 days and was monitored by NMR spectroscopy. Potassium carbonate (10 mg) was added, and the mixture was filtered into a base-washed flask and concentrated in vacuo to give 65 mg of crude product (81%). No further purification was done. The diyl trapping reaction was initiated immediately! TLC: the acetal was not stable to silica gel. IR (crude, neat, NaCl): 3010, 2940, 2850, 1450, 1350, 1120, 1050, 960, 860 cm^{-1}. ^1H NMR (crude, 500 MHz, $CDCl_3$): δ 5.28 (s with fine coupling, 1 H, J = 0.6, bridgehead H), 5.10 (s, 1 H, vinyl), 4.94 (s with fine coupling, 1 H, J = 1.5, bridgehead H), 4.77 (s with fine coupling, 1 H, J = 2.1, vinyl), 4.70 (t, 1 H, J = 7.5, vinyl), 4.52 (s, 1 H, $CH(OCH_3)_2$), 3.13 (s, 6 H, OCH_3), 2.00 (t, 2 H, J = 7.5, allylic H), 1.70 (m, 2 H, allylic), 1.36 (quintet, 2 H, J = 7.8, $CH_2CH_2CH_2$), 1.11 (m, 2 H, endo H), 0.83 (apparent d, 2 H, J = 7.5, exo H).

Diyl Trapping Reaction: Diazene Acetal 6 in THF. A solution of crude diazene acetal **6** (0.065 g, 0.26 mmol) in THF (173 mL, 1.5 mM) was degassed with argon for 45 min and refluxed for 4 h. Upon cooling to room temperature, concentration in vacuo, and chromatography on silica gel (the acetal trapped products were stable to chromatography conditions, 2 g, 5% Et_2O/SSF, 200 mL) 50 mg of trapped products was obtained (86% over two steps) in a ratio of 1.0:1.0:1.0 for cis,anti:exo:endo bridged products. The linear to bridged ratio was 1.0:2.0. The isomers were separated by HPLC (Axxiom column) using 2% Et_2O/hexane (flow rate: 3 mL/min) as the eluting solvent. The HPLC only separated the exo bridged product from the cis,anti and endo bridged isomers. Therefore, the mixture of the latter was deacetalized to aldehyde, separated on silica gel (1 g, 1% Et_2O/SSF, 200 mL), and acetalized again to complete the separation of all the isomers. The pertinent spectral data are reported below.

(3aβ,6aα,7aβ)-2,3,3a,5,6,6a,7,7a-Octahydro-7a-(dimethoxymethyl)-1*H*-cyclopenta[*a*]pentalene. TLC (2% Et_2O/SSF): R_f 0.10, *p*-anis. IR (neat, NaCl): 3020, 2960, 2860, 1450, 1350, 1200, 1140, 1060, 950, 800 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.19 (s, 1 H, vinyl), 4.07 (s, 1 H, C*H*[OCH_3]$_2$), 3.48 (s, 6 H, OCH_3), 3.01 (m, 1 H, allylic bridgehead on C_{6a}), 2.67 (apparent t, 1 H, *J* = 7, allylic bridgehead H on C_{3a}), 2.55 (m, 1 H, allylic H on C_5), 2.48 (m, 1 H, allylic H on C_5), 2.09 (dt, 1 H, *J* = 12.5, 13, H on C_6), 1.98 (dt, 1 H, *J* = 13, 14, H on C_3), 1.87 (m, 1 H, H on C_1), 1.74 (apparent dd, 1 H, *J* = 12.5, H on C_7), 1.59 (m, 2 H), 1.48–1.31 (m, 3 H), 1.27 (apparent t, 1 H, *J* = 11.5, H on C_7). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.63 (C_{4a}), 117.04 (C_4), 112.89 (C_8), 64.51 (C_{7a}), 57.77 (OCH_3), 49.87 (C_{6a}), 44.60 (C_{3a}), 42.51 (C_1), 37.30 (C_5), 36.12 (C_6), 34.77 (C_2), 32.27 (C_7), 27.50 (C_3). LRMS (CI, CH_4): *m/z* (rel int) 221 (M^+ + 1, 5), 191 (60), 159 (100), 133 (30), 95 (20), 75 (90), 69 (30). Exact mass [HRMS (CI)] calcd for $C_{14}H_{23}O_2$ (M^+ + 1) 223.1698, found 223.1698.

(3aα,4α,8α)-2,3,3a,4,5,6,7,8-Octahydro-4-(dimethoxymethyl)-4,6-methanoazulene. TLC (2% Et_2O/SSF): R_f 0.14, *p*-anis. IR (neat, NaCl): 3040, 2950, 2850, 1725, 1450, 1200, 1105, 1050, 960, 800, 740 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.50 (s, 1 H, vinyl), 3.99 (s, 1 H, C*H*(OCH_3)$_2$), 3.51, 3.48 (s, 6 H, OCH_3), 2.66 (m, 2 H, allylic bridgehead H on C_{3a} and C_{8a}), 2.41 (m, 1 H, allylic H on C_2), 2.17 (apparent ddd, 1 H, *J* = 4, allylic H on C_2), 2.0 (apparent quintet, 1 H, *J* = 5.5, H on C_3), 1.65–1.45 (m, 8 H), 1.41 (apparent d, 1 H, *J* = 10.5, exo H on C_9). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0 (C_{8a}), 120.82 (C_1), 112.30 (C_{10}), 58.77 (OCH_3), 57.45 (OCH_3), 53.85 (C_8), 45.0 (C_{3a}), 43.12 (C_2), 38.3 (C_4), 33.88 (CH_2), 33.82 (CH_2), 31.20 (CH_2), 30.02 (CH_2), 19.41 (C_6). LRMS (CI, CH_4): *m/z* (rel int) 221 (M^+ – 1, 5), 191 (100), 177 (20), 159 (50), 133 (20), 117 (20), 95 (20), 81 (30), 75 (60), 69 (60). Exact mass [HRMS (CI)] calcd for $C_{14}H_{23}O_2$ (M^+ + 1) 223.1698, found 223.1698.

(3aβ,4α,8α)-2,3,3a,4,5,6,7,8-Octahydro-4-(dimethoxymethyl)-4,6-methanoazulene. TLC (5% Et_2O/SSF): R_f 0.22, *p*-anis. IR (neat, NaCl): 3040, 2940, 2840, 1450, 1350, 1200, 1060, 960, 980, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.18 (m, 1 H, vinyl), 3.85 (s, 1 H, C*H*(OCH_3)$_2$), 3.48, 3.47 (s, 6 H, OCH_3), 2.84 (m, 1 H, allylic bridgehead H on C_{3a}), 2.70 (s, 1 H, allylic bridgehead H on C_8), 2.63 (m, 1 H, allylic H on C_2), 2.53 (m, 1 H, allylic H on C_2), 1.92 (m, 1 H, endo H on C_9), 2.00–1.30 (m, 10 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.46 (C_{8a}), 115.87 (C_1), 113.47 (C_{10}), 58.13 (OCH_3), 57.83 (OCH_3), 45.70 (C_{3a}), 37.08 (C_2), 33.90 (CH_2), 33.89 (CH_2), 29.70 (CH_2), 26.69 (CH_2), 25.96 (CH_2), 15.27 (C_6). LRMS (CI, CH_4): *m/z* (rel int) 221 (M^+ – 1, 2), 191 (100), 159 (50), 133 (20), 109 (20), 95 (30), 81 (20), 75 (40), 67 (40). Exact mass [HRMS (CI)] calcd for $C_{14}H_{21}O_2$ (M^+ – 1) 221.1542, found 221.1541.

Synthesis of Hydrocarbon 9. (3a*S,4*S**,7*R**,7a*S**)-Trimethyl[(2,3,3a,4,7,7a-hexahydro-4,7-methano-1*H*-inden-5-yl)oxy]silane.** The known TMS–enol ether was prepared by using the methodology of Stothers.[4] To a solution of diisopropylamine (3.44 g, 34 mmol) in THF (50 mL, 0.68 M) at 0 °C was added *n*-butyllithium (18.8 mL) via syringe over 10 min. After 20 min at 0 °C, the reaction mixture was cooled to −78 °C and *exo*-8-oxotricyclo[5.2.1.$0^{2,6}$]decane (3 g, 20 mmol) in THF (6 mL, 3 M) was added over 10 min via syringe. The reaction mixture was stirred for 0.5 h at this temperature, TMSCl (5.43 g, 50 mmol) was added, and the stirring was continued at −78 °C for 1 h. The reaction mixture was warmed to room temperature over 2 h, quenched with saturated aqueous $NaHCO_3$ (50 mL). The layers were separated, the aqueous layer was extracted with SSF (4 × 50 mL), and the combined organic layers were dried and concentrated in vacuo. The excess diisopropylamine was removed in vacuo (2 mm) to give 5.45 g of crude enol ether, which was 83% pure by capillary column GC. Further purification was not done since the TMS–enol ether reverts back to the starting material on silica gel. The spectral data were in accord with those reported by Stothers.[4]

(1a*R,2*S**,2a*S**,5a*R**,6*R**,6a*S**)-Trimethyl[(octahydro-2,6-methanocycloprop[*f*]inden-1a(1*H*)-yl)oxy]silane.** The cyclopropanation procedure of Stothers was utilized.[4] Zn was activated by washing Zn dust with 10% HCl, 95% EtOH, EtOH (200 proof), and benzene successively and drying in vacuo for 2 h followed by purging with nitrogen. Zn(Ag) couple was prepared by addition of activated Zn dust to a refluxing mixture of AgOAc (15 mg) in AcOH (5 mL) and refluxing the resulting mixture for 2 min; the mixture was cooled to room temperature, AcOH was removed, the Zn(Ag) was washed with Et_2O (4 × 10 mL) and dried in vacuo with gentle warming. Upon cooling to room temperature Et_2O (10 mL) and CH_2I_2 (7.22 g, 27 mmol) were added, the mixture was warmed until refluxing occurred without external heating. Upon cessation of reflux, the mixture was stirred at room temperature for 1 h, the crude TMS enol ether was added (in 40 mL of Et_2O), and the mixture was refluxed for 18 h. Pyridine (3.9 g, 49 mmol) was added at 0 °C, the reaction mixture was filtered and concentrated in vacuo, the residues were taken up in SSF, and the remaining solids were filtered. The filtrate was concentrated in vacuo to give 4.48 g of crude product. No further purification was conducted. The crude FTIR shows a mixture of the starting ketone, TMS–enol ether, as well as cyclopropanated product. The spectral data were in accord with those reported by Stothers.[4]

(3a*S,4*S**,8*R**,8a*S**)-1,2,3,3a,4,5,6,7,8,8a-Decahydro-4,8-methanoazulen-5-one.** The ring expansion was carried out as indicated by Stothers.[4] The crude mixture from the previous reaction was dissolved in MeOH (63 mL) and cooled to 0 °C. Then, NaOH (31 mL, 3 M) was added, and the reaction mixture was placed in the cold room (4 °C) and monitored by capillary column GC. After 18 h at 4 °C, the reaction mixture was concentrated in vacuo to remove methanol, the aqueous layer was extracted with Et_2O (3 × 30) and CH_2Cl_2 (3 × 30 mL), and the combined organic layers were washed with brine (40 mL), dried, and concentrated in vacuo to afford 3.25 g of crude product. Chromatography on silica gel (300 g; 5% Et_2O/SSF, 1000 mL; 10% Et_2O/SSF, 2000 mL) afforded 155.2 mg of the known ketone, which was 90% pure by capillary column GC; the impurity was the starting ketone. Enough ketone was isolated by preparative GC to carry on to the synthesis of hydrocarbon **9**. The spectral data were in accord with those reported by Stothers.[4]

(3a*S,4*R**,8*S**,8a*R**)-1,2,3,3a,4,5,6,7,8,8a-Decahydro-4,8-methanoazulene (9).** To a mixture of ketone 8 (95.4 mg, 0.58 mmol) in CH_2Cl_2 (2 mL, 0.28 M) was added 1,3-propanedithiol (87 μL, 0.87 M). The resulting mixture was cooled to 0 °C, and BF_3·Et_2O (21 μL, 0.18 mmol) was added (cloudy solution). After 5 min, the reaction mixture was brought to room temperature, stirred for 21 h, and then quenched with 2 N NaOH (2 mL). The layers were separated, the aqueous layer was extracted with Et_2O (4 × 20 mL), and the combined organic layers were washed with brine (30 mL), dried, and concentrated in vacuo to afford 139.1 mg of crude dithiane. Purification on silica gel (50 g, SSF, 500 mL, 20% Et_2O/SSF, 300 mL) gave 111.1 mg of product (79%), which was 93% pure by capillary column GC. TLC (100% SSF): R_f 0.4, *p*-anis. ^1H NMR (500 MHz, $CDCl_3$): δ 2.9–2.6 (m, 5 H), 2.2–1.5 (m, 14 H), 1.35 (m, 1 H), 1.25 (m, 1 H), 0.95 (m, 1 H). LRMS (EI): *m/z* (rel int) 254 (M^+, 85), 221 (15), 180 (65), 151 (70), 145 (100), 132 (18), 119 (27), 106 (23), 97 (14), 91 (45), 79 (70), 71 (24), 67 (43), 53 (22), 45 (30).

From a well-shaken bottle of Raney Ni (W-2), 0.8 mL of the suspension of Ra Ni in pH 10 buffer was removed and washed with EtOH (3 × 2 mL). Then, Ra Ni was transferred to the reaction flask with the aid of 4 mL of EtOH. The reaction mixture was warmed to 75 °C in an oil bath. Capillary column GC analysis indicated that the reaction ceased after 17 h. Therefore, the reaction mixture was filtered through Celite, concentrated in vacuo, and resubjected to Ra Ni desulfurization. After 58 h, the crude mixture was filtered on Celite, and the filter cake was washed with Et_2O. The spectral data for this known hydrocarbon were as follows.[14] LRMS (EI): *m/z* (rel int) 150 (M^+, 45), 135 (20), 121 (15), 108 (25), 93 (10), 82 (40), 79 (40), 67 (100), 54 (20), 51 (10). Exact mass [HRMS (EI)] calcd for $C_{11}H_{18}$ (M^+) 150.1409, found 150.1409.

Conversion of 12 to 9. (3a*R,4*S**,8*S**,8a*R**)-1,2,3,3a,4,5,6,7,8,8a-Decahydro-4,8-methanoazulene-4-methanol.** To a solution of exo isomer **12** (14 mg, 0.079 mmol) in benzene (0.5 mL, 0.16 M) at room temperature was added PtO_2

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(2 mg). The reaction flask was purged with hydrogen, placed under a positive pressure of hydrogen, and monitored by capillary column GC and TLC. After 20 min, the mixture was filtered through Celite and concentrated in vacuo to give 12.5 mg of reduced product. No further purification was required. TLC (20% Et_2O/SSF): R_f 0.26, *p*-anis. FTIR (crude, neat, NaCl): 3376–3063, 2922, 2854, 1443 cm^{-1}. ^1H NMR (crude, 500 MHz, $CDCl_3$): δ 3.55 (d, 1 H, J = 18.0, CH_2OH), 3.46 (d, 1 H, J = 18.0, CH_2OH), 2.2–0.8 (m, integrates for 18 H). LRMS (EI): *m/z* (rel int) 162 ($M^+ - H_2O$, 45), 149 (100), 133 (12), 119 (15), 106 (22), 93 (43), 81 (68), 77 (28), 76 (75), 55 (28), 51 (9), 43 (8). Exact mass [HRMS (EI)] calcd for $C_{12}H_{20}O$ 180.1514, found 180.1514.

(3a*R,4*S**,8*S**,8a*R**)-1,2,3,3a,4,5,6,7,8,8a-Decahydro-4,8-methanoazulene-4-carboxylic Acid.** This compound was synthesized using two different routes.

A. To reduced exo isomer (12.8 mg, 0.071 mmol) dissolved in a mixture of CCl_4:H_2O:CH_3CN (1:1.5:1 v/v, 1.75 mL) at 0 °C was added $NaIO_4$ (62 mg, 0.29 mmol) and a catalytic amount of $RuCl_3 \cdot H_2O$ (1 mg, black suspension). The reaction mixture was warmed to room temperature and monitored by capillary column GC. After 45 min, the reaction mixture was diluted with Et_2O (5 mL) and H_2O (5 mL), the layers were separated, the aqueous layer was extracted with Et_2O (4 × 20 mL), and the combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residues were taken up in Et_2O (gray solution), filtered through Celite, and concentrated in vacuo to give 32.3 mg of the crude acid which was 92% pure by capillary column GC. No further purification was done.

B. To a solution of exo ketone isomer **16** (0.0063 g, 0.032 mmol) in 1,4-dioxane (1 mL, 0.032 M) was added 10% aqueous NaOH (0.5 mL) and enough KI/I_2 solution (0.5 g of KI and 0.25 g of I_2 in 2 mL of H_2O) to make the mixture colored (iodine color). Upon warming to 60° C, the color disappeared; more KI/I_2 solution was added. This process was repeated until the color of iodine did not disappear. The excess I_2 was removed by the addition of 10% NaOH (0.1 mL). After being stirred for an additional 20 min, the solution was acidified with 10% aqueous HCl (1 mL), causing the formation of I_2 once again (reddish brown). Excess I_2 was removed by the addition of $Na_2S_2O_3$ (2 mL, 0.1 M), the layers were separated, the aqueous layer was extracted with Et_2O (3 × 5 mL), and the combined organic layers were washed with brine (5 mL), dried on Na_2SO_4, and concentrated in vacuo to afford 4 mg of crude acid (64%). No further purification was carried out. TLC: The TLC plate did not stain under a variety of staining conditions. FTIR (crude, neat, NaCl) 3393–2500, 2945, 2857, 1694, 1459, 1292 cm^{-1}. ^1H NMR (crude, 500 MHz, $CDCl_3$): δ 2.4 (m, 1 H), 2.20 (m, 1 H), 1.90 (m, 1 H), 1.60–1.0 (m, 14 H). LRMS (EI): *m/z* (rel int) 194 (M^+, 25), 176 (40), 149 (20), 126 (60), 108 (20), 91 (30), 81 (50), 77 (40), 67 (100), 53 (40), 45 (20). Exact mass [HRMS (EI)] calcd for $C_{12}H_{18}O_2$ (M^+) 194.1307, found 194.1306.

(3a*S,4*R**,8*S**,8a*R**)-1,2,3,3a,4,5,6,7,8,8a-Decahydro-4,8-methanoazulene (9).** To a solution of acid (32.3 mg, 0.16 mmol) in PhH (1 mL, 0.16 *M*) at room temperature were added K_2CO_3 (23 mg, 0.16 mmol) and oxalyl chloride (17 μL, 0.19 mmol). To this heterogeneous mixture was added a drop of DMF. After 10 min "one crystal" of 4-(dimethylamino)pyridine, sodium 2-mercaptopyridine *N*-oxide (27 mg, 0.18 mmol yellow solution), and *tert*-butylmercaptan (93 μL, 0.83 mmol) were added via syringe, and the mixture was refluxed. After 4 h, the reaction mixture was cooled to room temperature and filtered through Florisil. Capillary column GC co-injection of this product and hydrocarbon **9** on two different capillary columns, as well as a comparison of GCMS data, revealed their identity. The spectral data for this known hydrocarbon were as follows.[14] LRMS (EI) *m/z* (rel int) 150 (60), 135 (30), 121 (30), 108 (60), 93 (30), 82 (70), 79 (20), 67 (100), 55 (35), 51 (10). Exact mass [HRMS (EI)] calcd for $C_{11}H_{18}$ (M^+) 150.1409, found 150.1408.

Synthesis of Endo Ketone 10. (3a*S,4*R**,7*S**,7a*R**)-2,3,3a,4,7,7a-Hexahydro-4,7-methano-1*H*-inden-1-one.** A modification of Dilling's procedure was used for synthesis of this compound.[15] To a mixture of cyclopentenone (0.98 g, 11.9 mmol) and cyclopentadiene (1.2 g, 17.9 mmol) in Et_2O (12 mL, 1 M) at 0 °C was added a catalytic amount of $BF_3 \cdot Et_2O$ (0.59 mL, 4.8 mmol) over 5 min via syringe. The mixture was stirred while the cooling bath was warming to room temperature. After 24 h, H_2O (10 mL) was added, the layers were separated, the aqueous layer was extracted with Et_2O (5 × 20 mL), and the combined organic layers washed with brine (30 mL), dried, and concentrated in vacuo to afford 1.98 g of crude product. Upon chromatography on silica gel (200 g; 5% EtOAc/SSF, 1000 mL; 20% EtOAc/SSF, 500 mL) 1.7 g of pure cycloadduct was obtained (97%). TLC (10% EtOAc/SSF): R_f 0.42, *p*-anis. The spectral data were in accord with the values reported in the literature.[15]

(1*R,3a*S**,4*R**,7*S**,7a*R**)-2,3,3a,4,7,7a-Hexahydro-4,7-methano-1*H*-inden-1-ol.**[16] To a suspension of $LiAlH_4$ (0.74 g, 19.64 mmol) in Et_2O (58 mL, 0.2 M) at 0 °C was added the Diels–Alder cycloadduct (1.7 g, 11.5 mmol) via syringe over 5 min. The reaction mixture was allowed to reach the room temperature and was monitored by TLC. After 1.5 h, the reaction mixture was cooled to 0 °C, quenched with MeOH (10 mL), diluted with Rochelle salt (100 mL), and stirred vigorously at room temperature until two distinct layers were apparent (1 h). The layers were separated, the aqueous layer was extracted with Et_2O (5 × 30 mL), and the combined organic layers were washed with brine (30 mL), dried, and concentrated in vacuo to give 1.6 g of crude alcohol which was 99% pure by capillary column GC. No further purification was conducted. TLC (60% Et_2O/SSF): R_f 0.46, $KMnO_4$. The spectral data were in accord with the values reported in the literature.[15a,b,16]

(1*R,3a*S**,4*R**,7*S**,7a*R**)-2,3,3a,4,7,7a-Hexahydro-1-((methylsulfonyl)oxy)-4,7-methano-1*H*-indene.** To a solution of the crude alcohol (1.6 g, 10.4 mmol) and Et_3N (1.6 g, 15.6 mmol) in CH_2Cl_2 (52 mL, 0.2 M) at −5 °C was added MsCl (1.3 g, 11.4 mmol) via syringe over 5 min. After 0.5 h, the mixture was washed with H_2O (30 mL), cold 10% aqueous HCl (30 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL), dried, and concentrated in vacuo to give 2.5 g of crude mesylate which was 97% pure by capillary column GC. No further purification was conducted. TLC (50% Et_2O/SSF): R_f 0.46, *p*-anis. FTIR (crude, neat, NaCl): 2972, 2870, 1465, 1336, 1175, 970, 902, 868, 740 cm^{-1}. ^1H NMR (crude, 300 MHz, $CDCl_3$): δ 6.2 (m, 2 H, vinyl), 5.0 (apparent q, 1 H, J = 9, H on C_1), 3.1–2.6 (m, 7 H), 2.0–1.2 (m, 6 H). LRMS (CI, CH_4): *m/z* (rel int) 133 ($M^+ - MsOH_2$, 15), 117 (8), 105 (8), 95 (6), 91 (18), 79 (5), 67 (100).

(3a*R,4*S**,7*R**,7a*S**)-2,3,3a,4,7,7a-Hexahydro-4,7-methano-1*H*-indene.**[17] To a suspension of LAH (0.61 g, 16.2 mmol) in Et_2O (54 mL, 0.2 M) at 0 °C was added via cannula over 5 min the crude mesylate (2.5 g, 10.8 mmol); the solution was warmed to room temperature. After 3 h, the reaction was quenched with ice chips and diluted with Rochelle's salt (100 mL). The mixture was stirred vigorously until two distinct layers were apparent (1.5 h), the layers were separated, the aqueous layer was extracted with Et_2O (6 × 80 mL), and the combined organic layers were washed with brine (100 mL), dried, and concentrated in vacuo to give 1.3 g of crude product. Upon chromatography on silica gel (100 g; SSF, 800 mL) 1.11 g of pure olefin was obtained (77% over three steps). TLC (SSF): R_f 0.74, I_2, $KMnO_4$. The spectral data were in accord with the values reported in the literature.[17]

(3a*R,4*S**,5*R**,7*S**,7a*R**)-2,3,3a,4,5,6,7,7a-Octahydro-5-hydroxy-4,7-methano-1*H*-indene.**[18] To a solution of olefin (1.11 g, 8.32 mmol) in THF (17 mL, 0.5 M) at 0 °C was added BH_3·DMS (0.95 g, 12.4 mmol) via syringe over 5 min. The resulting solution

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was warmed to the room temperature, stirred for 4 h, cooled to 0 °C, and quenched with 2 N aqueous NaOH (4 mL). After 5 min, 30% H_2O_2 (4 mL) was added, and the reaction mixture was stirred at reach room temperature overnight. Water (30 mL) was added, the aqueous layer was extracted with Et_2O (6 × 30 mL), and the combined organic layers were washed with brine (50 mL), dried, and concentrated in vacuo to give 1.5 g of crude alcohol. Upon chromatography on silica gel (60% Et_2O/SSF, 1300 mL), 968 mg of the alcohol was obtained (77%). TLC (60% Et_2O/SSF): R_f 0.7, I_2, $KMnO_4$. The spectral data were in accord with the literature.[18]

(3a*R,4*S**,7*S**,7a*R**)-2,3,3a,4,5,6,7,7a-Octahydro-4,7-methano-1*H*-inden-5-one (10).**[4,18] To a solution of alcohol (0.998 g, 6.6 mmol) in CH_2Cl_2 (198 mL, 0.1 M) at room temperature was added pyridinium chlorochromate (4.26 g, 19.8 mmol) and Celite (5 g); the mixture was stirred for 3 h. Et_2O (200 mL) was added to precipitate the chromium residues. Upon filtration through Florsil and chromatography on silica gel (200 g; 20% Et_2O/SSF, 500 mL) 840.1 mg of pure compound **10** was obtained (84%). TLC (60% Et_2O/SSF): R_f 0.63, I_2, *p*-anis. The spectral data were in accord with the values reported in the literature.[4,18]

Conversion of Endo Ketone 10 to Hydrocarbon 11. (3a*R,4*S**,7*R**,7a*R**)-Trimethyl[(2,3,3a,4,7,7a-hexahydro-4,7-methano-1*H*-inden-5-yl)oxy]silane.**[4] The same procedure as reported for the synthesis of TMS–enol ether for the exo isomer was followed with 0.840 g of compound **10** as starting material. The crude product was 71% pure by a capillary column GC. No further purification was done since the product reverts back to the starting material on silica gel. The spectral data were in accord with those reported by Stothers.[4]

(1a*R,2*S**,2a*R**,5a*S**,6*R**,6a*S**)-Trimethyl[(octahydro-2,6-methano-1*H*-cycloprop[*f*]inden-1a-yl)oxy]silane.**[4] The same procedure as reported for the cyclopropanation of the exo isomer was followed to afford 2 g of crude product, which was taken on to the next step without further purification. The spectral data were in accord with those of Stothers.[4]

(3a*R,4*R**,8*R**,8a*R**)-1,2,3,3a,4,5,6,7,8,8a-Decahydro-4,8-methano-1*H*-azulen-5-one.**[4] The same procedure as reported for the exo isomer was followed. Enough of ketone was isolated by preparative GC for conversion to hydrocarbon **11**. The spectral data were in accord with those reported by Stothers.[4]

(3a*R,4*S**,8*S**,8a*S**)-1,2,3,3a,4,5,6,7,8,8a-Decahydro-4,8-methanoazulene (11).** The same procedure as described for the synthesis of the exo isomer **9** was followed starting with 45 mg (0.27 mmol) of endo ketone. TLC (100% SSF): R_f 0.38 *p*-anis. The spectral data for the dithiane intermediate were as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 3–2.3 (m, 8 H), 2.2–1.8 (m, 7 H), 1.7–1.2 (m, 7 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 49, 47, 45, 40, 35, 32, 31, 27.2, 27.1, 26, 25.3, 25.1, 24.7. LRMS (EI): *m/z* (rel int) 254 (M^+, 40), 180 (35), 146 (100), 131 (10), 119 (20), 106 (20), 91 (30), 79 (45), 67 (45), 53 (15). Exact mass [HRMS (EI)] calcd for $C_{14}H_{22}S_2$ (M^+) 254.1163, found 254.1123.

Upon Ra Ni desulfurization of the dithiane, hydrocarbon **11** was obtained. The spectral data for this known hydrocarbon were as follows.[14] LRMS (EI): *m/z* (rel int) 150 (M^+, 25), 135 (10), 121 (10), 108 (15), 93 (20), 82 (80), 79 (30), 67 (100), 54 (30), 51 (10). Exact mass [HRMS (EI)] calcd for $C_{11}H_{18}$ (M^+) 150.1409, found 150.1408.

Conversion of Endo Isomer 13 to Hydrocarbon 11. (3a*S,4*S**,8*S**,8a*S**)-1,2,3,3a,4,5,6,7,8,8a-Decahydro-4-(hydroxymethyl)-4,8-methanoazulene.** The same procedure as described for the hydrogenation of exo isomer **12** was followed starting with 16.4 mg of **13**, which was 77% pure by capillary column GC, the impurity was the exo isomer **12**. TLC (20% Et_2O/SSF): R_f 0.26, *p*-anis. FTIR (crude, neat, NaCl): 3685–3038, 2913, 2856, 1462, 1035 cm^{-1}. ^1H NMR (crude, 300 MHz, $CDCl_3$): δ 3.4 (s, 2 H), 2.6 (m, 1 H), 2.2 (m, 2 H), 2.0 (m, 2 H), 1.8–1.1 (m, 13 H). LRMS (EI): *m/z* (rel int) 162 ($M^+ - H_2O$) 162 (45), 149 (80), 134 (25), 119 (20), 108 (30), 93 (70), 81 (100), 77 (30), 67 (90), 55 (30), 51 (10). Exact mass [HRMS (EI)] calcd for $C_{12}H_{18}$ ($M^+ - H_2O$) 162.1409, found 162.1408.

(3a*S,4*S**,8*S**,8a*S**)-1,2,3,3a,4,5,6,7,8,8a-Decahydro-4-carboxy-4,8-methanoazulene.** This compound was synthesized using two different routes. **A.** The Sharpless oxidation as reported for exo isomer was followed starting with 15 mg of crude endo alcohol (78% pure by a capillary column GC). The impurity was the exo alcohol. **B.** The iodoform reaction as reported for exo ketone **16** was followed starting with 3.5 mg of endo ketone **16**. FTIR (crude, neat, NaCl): 3353–2375, 2944, 1690, 1459, 1255 cm^{-1}. ^1H NMR (crude, 500 MHz, $CDCl_3$): δ 3.0–0.50 (m). LRMS (CI, CH_4): *m/z* (rel int) 195 (M^+, 20), 177 (10), 161 (30), 149 (30), 135 (20), 123 (22), 109 (30), 95 (15), 91 (15), 81 (45), 69 (100). Exact mass [HRMS (CI)] calcd for $C_{12}H_{19}O_2$ ($M^+ + 1$) 195.1385, found 195.1385.

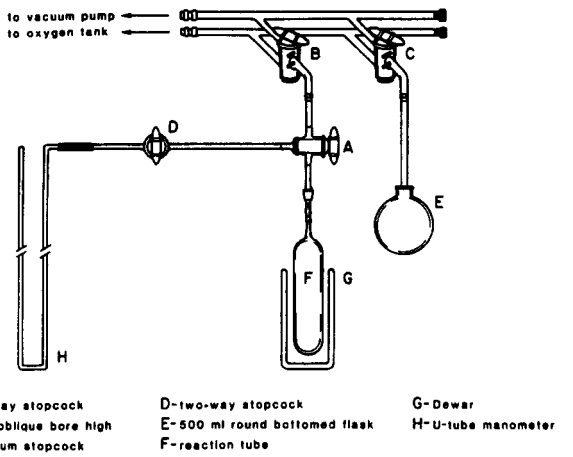

Figure 1. Apparatus used in oxygen quenching studies.

(3a*R,4*R**,8*S**,8a*S**)-1,2,3,3a,4,5,6,7,8,8a-Decahydro-4,8-methanoazulene (11).** The Barton decarboxylation as reported for the synthesis of compound **9** was followed starting with 13 mg of crude endo acid which was 74% pure by a capillary column GC. The impurity is the exo acid. The capillary column GC co-injection on two different columns as well as GCMS of this hydrocarbon are exactly the same as the hydrocarbon obtained from the Ra Ni desulfurization of the endo dithiane. The spectral data for this known hydrocarbon were as follows.[14] LRMS (EI): *m/z* (rel int) 150 (M^+, 40), 108 (30), 93 (30), 82 (100), 67 (100), 55 (35). Exact mass [HRMS (EI)] calcd for $C_{11}H_{18}$ (M^+) 150.1409, found 150.1408.

Diyl Trapping Reaction in the Presence of Oxygen. For the oxygen quenching experiments, the apparatus depicted schematically in Figure 1 was used. The 500-mL round-bottomed flask was evacuated and purged with oxygen. This cycle was repeated three times and after the third time, stopcock C was closed so that the flask contained oxygen. A 1.5 mM solution of the diazene in CH_3CN was prepared. The sample tube was inserted in a Dewar, cooled to −78 °C (dry ice/acetone), and evacuated (stopcock B set to the pump side, ca. 3 Torr). Then the tube was purged with oxygen (stopcock B set to the oxygen side). This cycle was repeated three times, and after the fourth evacuation, stopcock D was opened slowly to the system so that the manometer could be adjusted to the pressure of the system (3 Torr). Then stopcock C was opened to allow oxygen into the delivery tube; stopcock B was opened slowly to the tube while adjusting the pressure inside the tube to 200 Torr of oxygen. All stopcocks were closed, and the tube was sealed. The vapor over such a bath will not ordinarily ignite even when a flame is "played" over it, but the flame should not come in contact with the liquid adhering to the side of the tube. The tube was warmed to room temperature, placed it in a constant temperature bath set at 70 °C for 9 h, cooled to room temperature, concentrated, and analyzed by capillary column GC to determine the yield; *n*-$C_{13}H_{28}$ was used as an internal standard.

For comparison, the reaction was also carried out in a sealed tube in the absence of oxygen. For these experiments, the tube was subjected to the freeze–pump-thaw degassing (4 cycles) procedure and sealed. After heating to 70° C for 9 h and concentration, the products were analyzed by capillary column GC for the total yield of all isomers, the yield of linearly fused tricyclopentanoids, and the yield of bridged products. Yields represent an average over two sets of experiments and two to six GC injections.

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Registry No. **4**, 125877-64-7; **5**, 125877-59-0; **6**, 125877-74-9; **7**, 125877-65-8; **8**, 34748-64-6; **8** dithiane derivative, 125877-70-5; **9**, 53495-28-6; **10**, 31351-12-9; **10** dithiane derivative, 125949-38-4; **11**, 54676-38-9; **12**, 125877-61-4; **13**, 125949-32-8; **16** (exo isomer), 126059-67-4; **16** (endo isomer), 125877-67-0; methallyl alcohol, 513-42-8; 6-(*tert*-butyldimethylsiloxy)-2-methylidenehexan-1-ol, 125877-52-3; 1-(benzoyloxy)-2-methylidene-6-(*tert*-butyldimethylsiloxy)hexane, 125877-53-4; 1-(benzoyloxy)-2-methylidenehexan-6-ol, 125877-54-5; 1-(benzoyloxy)-2-methylidenehexan-6-al, 125877-55-6; 6-(4-((benzoyloxy)methyl)-4-pentenyl)fulvene, 125877-56-7; dimethyl 2,3-diazo-7-(5′-((benzoyloxy)methyl)hex-5′-enylidene)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate, 125877-57-8; dimethyl 2,3-diaza-7-(5′-((benzoyloxy)methyl)hex-5′-enylidene)bicyclo[2.2.1]heptane-2,3-dicarboxylate, 125877-58-9; (3aα,6aα,7aβ)-2,3,3a,5,6,6a,7,7a-octahydro-1*H*-cyclopenta[*a*]pentalene-7a-methanol, 125877-60-3; (3aα,6aβ,7aβ)-2,3,3a,5,6,6a,7,7a-octahydro-1*H*-cyclopenta[*a*]pentalene-7a-methanol, 125949-33-9; 2,3-diaza-7-[5′-formyl-5′-methylidenepentanylidene]bicyclo[2.2.1]hept-2-ene, 125877-62-5; 2,3-diaza-7-(5′-methylene-6′-hydroxyheptanylidene)bicyclo-[2.2.1]hept-2-ene, 125877-63-6; ((3aβ,6aα,7aβ)-2,3,3a,5,6,6a,7,7a-octahydro-1*H*-cyclopenta[*a*]pentalen-7a-yl)-1-ethanone, 125877-66-9; ((3aα,6aα,7aα)-2,3,3a,5,6,6a,7,7a-octahydro-1*H*-cyclopenta-[*a*]pentalen-7a-yl)-1-ethanone, 125949-34-0; (3aα,6aα,7aβ)-2,3,3a,5,6,6a,7,7a-octahydro-7a-(dimethoxymethyl)-1*H*-cyclopenta[*a*]pentalene, 125877-68-1; (3aα,4aα,8α)-2,3,3a,4,5,6,7,8-octahydro-4-(dimethoxymethyl)-4,6-methanoazulene, 125877-69-2; (3aβ,4α,8α)-2,3,3a,4,5,6,7,8-octahydro-4-(dimethoxymethyl)-4,6-methanoazulene, 125949-35-1; (3a*S**,4*S**,7*R**,7a*S**)-trimethyl-[(2,3,3a,4,7,7a-hexahydro-4,7-methano-1*H*-inden-5-yl)oxy]silane, 85652-69-3; (1a*R**,2*S**,2a*S**,5a*R**,6*R**,6a*S**)-trimethyl[(octahydro-2,3-methano-1*H*-cycloprop[*f*]inden-1a-yl)oxy]silane, 125949-36-2; (3a*S**,4*S**,8*R**,8a*S**)-1,2,3,3a,4,5,6,7,8,8a-decahydro-4,8-methanoazulen-5-one, 53432-49-8; (3a*R**,4*S**,8*S**,8a*R**)-1,2,3,3a,4,5,6,7,8,8a-decahydro-4,8-methanoazulene-4-methanol, 125877-71-6; (3a*R**,4*S**,8*S**,8a*R**)-1,2,3,3a,4,5,6,7,8,8a-decahydro-4,8-methanoazulene-4-carboxylic acid, 125877-72-7; (3a*S**,4*R**,7*S**,7a*R**)-2,3,3a,4,7,7a-hexahydro-4,7-methano-1*H*-inden-1-one, 22981-84-6; (1*R**,3a*S**,4*R**,7*S**,-7a*R**)-2,3,3a,4,7,7a-hexahydro-4,7-methano-1*H*-inden-1-ol, 65470-96-4; (1*R**,3a*S**,4*R**,7*S**,7a*R**)-2,3,3a,4,7,7a-hexahydro-1-((methylsulfonyl)oxy)-4,7-methano-1*H*-indene, 125877-73-8; (3a*S**,4*R**,7*S**,7a*R**)-2,3,3a,4,7,7a-hexahydro-4,7-methano-1*H*-indene, 2826-19-9; (3a*R**,4*S*,5*R**,7*S**,7a*R**)-2,3,3a,4,5,6,7,7a-octahydro-5-hydroxy-4,7-methano-1*H*-indene, 10271-45-1; (3a*R**,4*S**,7*R**,7a*R**)-trimethyl[(2,3,3a,4,7,7a-hexahydro-4,7-methano-1*H*-inden-5-yl)oxy]silane, 85700-83-0; (1a*R**,2*S**,2a*R**,5a*S**,6*R**,6a*S**)-trimethyl[(octahydro-2,6-methano-1*H*-cycloprop[*f*]inden-1a-yl)oxy]silane, 125949-37-3; (3a*R**,4*S**,8*R**,8a*R**)-1,2,3,3a,4,5,6,7,8,8a-decahydro-4,8-methanoazulen-5-one, 85700-85-2; (3a*S**,4*S**,8*S**,8a*S**)-1,2,3,3a,4,5,6,7,8,8a-decahydro-4-(hydroxymethyl)-4,8-methanoazulene, 125949-39-5; (3a*S**,4*S**,8*S**,8a*S**)-1,2,3,3a,4,5,6,7,8,8a-decahydro-4-carboxy-4,8-methanoazulene, 125949-40-8; *trans*-2-[2-(hydroxymethyl)-2-methylenecyclopentyl]cyclopentenyl diradical, 125926-41-2; *trans*-2-[2-(dimethoxymethyl)-2-methylenecyclopentyl]cyclopentenyl diradical, 125926-43-4; *trans*-2-[2-(1,1-dimethoxyethyl)-2-methylenecyclopentyl]cyclopentenyl diradical, 125926-45-6; 1-(hydroxymethyl)-3-(5-cyclopentene-2,1-diyl)cyclohexyl diradical, 125926-42-3; 1-(dimethoxymethyl)-3-[5-cyclopetene-2,1-diyl)cyclohexyl diradical, 125926-44-5; 1-(1,1-dimethoxyethyl)-3-(5-cyclopentene-2,1-diyl)cyclohexyl diradical, 125926-46-7.

Supplementary Material Available: ^1H and ^{13}C NMR spectra (22 pages). Ordering information is given on any current masthead page.

C-Pivot Lariat Ethers Bearing an Electron-Donating Side Arm as Li^+-Selective Extractants

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A new series of methyl-substituted lariat ethers having a 12-, 13-, or 14-crown-4 ring was prepared by the reaction of the corresponding bromomethyl methyl crown ethers (**1-3**), with an appropriate sodium alkoxide or potassium phenoxide. Their complexation properties toward alkali metal cations were evaluated by the solvent extraction method. The lariat ether based on 13-crown-4 with a quinolinyloxy side arm (**5a**) shows a good affinity toward lithium cation over other alkali metal cations. The high extraction efficiency of **5a** was ascertained by comparing its extraction equilibrium constant (K_{ex}) with those of some representative compounds known as good extractants for lithium ion. The relationship between the structure of the ligand and the cation selectivity is also discussed.

Introduction

Lariat ethers show different complexation properties from normal crown ethers toward a variety of cations because of effective coordination of the electron-donating side arm.[1] Recently, we found that complexing ability toward Na^+ and Na^+/K^+ selectivity was dramatically raised by introducing a methyl group on the pivot position of Gokel's C-pivot lariat ether having a 15-crown-5 ring.[2] One of these lariat ethers having an 18-crown-6 ring displayed a higher stability constant for K^+ than an unsubstituted 18-crown-6.[2c]

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