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From Dimerization, to Cycloaddition, to Atom Transfer Cyclization: The Further Chemistry of TMM Diradicals†

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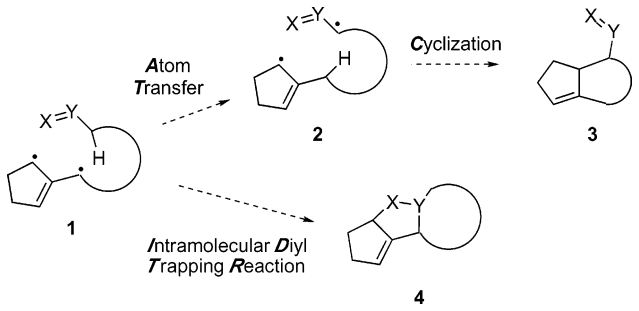
We describe [a] the first examples of *intra*molecular cycloaddition of a TMM diyl to a remotely tethered aldehyde, [b] the effect of a Lewis acid upon the course of TMM chemistry, [c] examples of exclusive intramolecular cycloaddition, competitive cycloaddition and ATC, and exclusive ATC, and [d] a set of predictive guidelines with which to assess whether cycloaddition or ATC will be the preferred path, and when the two processes will be competitive. Remarkably, a wide variety of structures can be obtained simply by varying the length of the tether within the diazenes investigated. DFT calculations were used to probe the energy surfaces for both atom transfer and cycloaddition. The transition structure for atom transfer involving the captodative system indicates that it occurs earlier along the reaction coordinate than for a system having only one radical stabilizing group. This is consistent with the existence of an exothermic process leading from the initial diyl to the captodatively stabilized distonic diyl. Gratifyingly, theory agrees with observation and provides substantial insight into the chemistry.

Introduction

Cyclopentatrimethylenemethane diradicals **1** (cyclopentaTMM diyls) can be intercepted *inter*molecularly by alkenes, alkynes, allenes, azodicarboxylates, and oxygen, as well as certain aldehydes, ketones, imines, and thioketones.[1] In so doing, both carbo- and heterocyclic systems can be constructed. These versatile intermediates also undergo a process we refer to as "atom transfer cyclization" (ATC).[2] This sequence has been less thoroughly explored than cycloaddition, and has only once been applied to total synthesis.[3] We wondered whether there were circumstances wherein ATC and the more thoroughly investigated intramolecular cycloaddition (IDTR: *i*ntramolecular *d*iyl *tr*apping *r*eaction)[4] might be competitive, and whether it was possible to determine circumstances under which one or the other of these reaction pathways would dominate (note Scheme 1). In this paper we describe [a] the first examples of *intra*molecular cycloaddition of a TMM diyl to a remotely tethered aldehyde, [b] the effect of a Lewis acid upon the course of TMM chemistry, [c] examples of exclusive intramolecular cycloaddition, competitive cycloaddition and ATC, and exclusive ATC, and [d] a set of predictive guidelines with which to assess whether cycloaddition or ATC will be the preferred path, and when the two processes will be competitive.

SCHEME 1



Four diyls, **9**−**12**, differing in the length of the methylene chain, *n*, and the nature of X, were studied. Their diazene precursors, **5**−**8**, were synthesized in the manner portrayed in Scheme 2. As we have described previously,[4] the routes have four integral components: (1) assembly of the alkyl chain, (2) fulvene formation, (3) Diels−Alder cycloaddition, and (4) conversion of a biscarbamate to a diazene linkage. Details are illustrated in Scheme 2 and described in the Experimental Section.

† We dedicate this paper to Professor Jerome Berson—friend, mentor, and the founder of cyclopenta TMM diradical research—on the occasion of his 80th birthday.

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(1) (a) Little, R. D.; Bode, H.; Stone, K. J.; Wallquist, O.; Dannecker, R. *J. Org. Chem.* **1985**, *50* (13), 2400. (b) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 4.

(2) (a) Billera, C. F.; Little, R. D. *J. Am. Chem. Soc.* **1994**, *116* (12), 5487. (b) Byers, J. Atom Transfer Reactions. In *Radicals In Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: New York, 2001; Vol. 1, Chapter 1.5. (c) Feray, L.; Kuznetsov, N.; Renaud, P. Hydrogen Atom Abstraction. In *Radicals In Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: New York, 2001; Vol. 1, Chapter 3.6.

(3) Carroll, G. L.; Allan, A. K.; Schwaebe, M. K.; Little, R. D. *Org. Lett.* **2000**, *2* (16), 2531.

(4) (a) Allan, A. K.; Carroll, G. L.; Little, R. D. *Eur. J. Org. Chem.* **1936**, *1*, 1. (b) Little, R. D. *Chem. Rev.* **1996**, *96* (1), 93.

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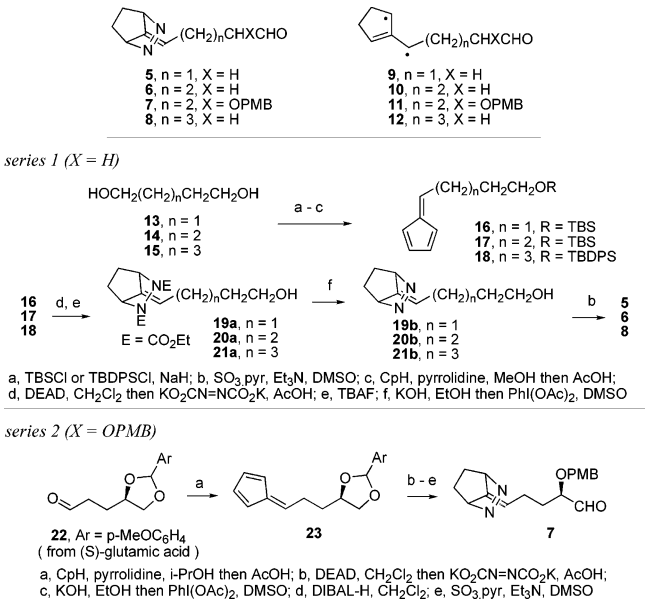
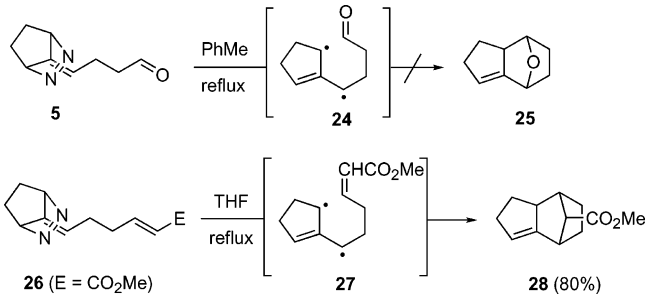
SCHEME 2



Results and Discussion

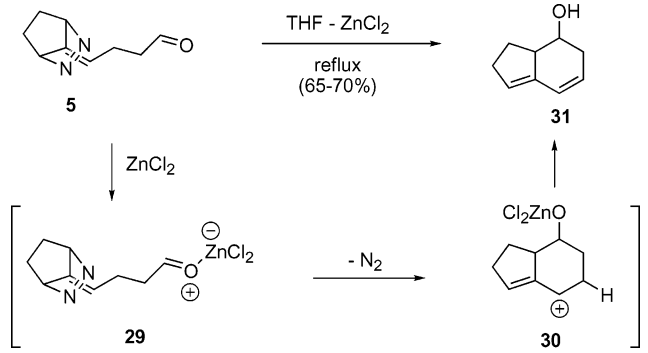
In each instance, the TMM diyl was generated by adding the precursor diazene to a refluxing solution of toluene. When $n = 1$ and X = H (viz., diazene **5**), diyl dimerization occurs. The tether is simply too short to allow the requisite centers to attain a geometry that is suitable for atom transfer (vide infra). That cycloaddition was not observed is presumably a reflection of the difference between the π-bond strength of a C=O vs a C=C bond, or a reversible cyclization of **24**.[5a] This conjecture is corroborated by the fact that the analogous diyl **27** containing a C−C π-bond in place of the carbonyl does undergo cycloaddition.[5b]

SCHEME 3



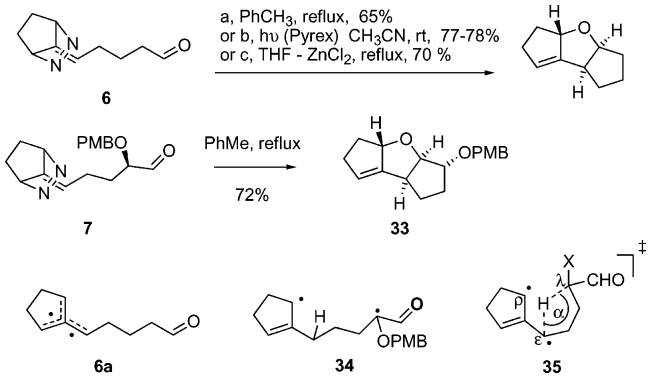
Interestingly, this limitation can be overcome by using a Lewis acid.[6] Thus, when heated to reflux in THF containing zinc chloride, **5** is smoothly converted to the [4.3.0] diene alcohol **31** in yields of 65−70%. Clearly complexation of the Lewis acid to the carbonyl oxygen now renders the unit susceptible to attack. We suspect that the product is formed via the attack of a dipolar diyl (a species with more dipolar character than diradical)[7] upon the polarized carbonyl unit to afford **30**, which subsequently collapses to form **31**.

SCHEME 4



In contrast to the dimerization that is observed in the chemistry of the diyl derived from **5**, cycloaddition *does occur* when the length of the tether is increased by one methylene unit. Thus, diazene **6** ($n = 2$, X = H) smoothly and efficiently undergoes cycloaddition. Atom transfer is *not* observed. The reaction can be conducted thermally (in the presence or absence of zinc chloride) or photochemically (450 W Hanovia, Pyrex filter, acetonitrile), the latter being the cleaner and more efficient process (77−78% vs 65%). Cycloaddition rather than atom transfer is also the case starting from the more elaborate diazene **7**, despite the fact that atom transfer would have afforded a captodatively stabilized diradical **34**.[8] That it did not occur is consistent with the inability of diyl **35** to achieve an "appropriate" transfer angle, α (see **35**, and note the discussion that occurs later), between either C_ρ or C_ϵ and the hydrogen to be transferred. Once again the tether is too short. In both instances (viz., with **6** and **7**) it is ideal for the formation of a five-membered ring, and this is the pathway that is observed.

SCHEME 5



To investigate these issues further we conducted DFT calculations using the UB3LYP/6-31G* basis set to probe

(5) (a) A reviewer has offered a reasonable alternative explanation. The rationale posits that a reversible cyclization of **24** would lead to an unstabilized oxygen-centered radical that would quickly revert to **24**. In contrast, both the cyclization of **27** and **29** would afford a stabilized radical. Perhaps, as the reviewer suggested, stabilization increases the lifetime of the intermediate enough to allow formation of the second σ-bond to occur. (b) Campopiano, O.; Little, R. D.; Petersen, J. L. *J. Am. Chem. Soc.* **1985**, *107* (12), 3721.

(6) The transformations appearing in this paper represent the first reported examples of the use of Lewis acids in conjunction with TMM diyl chemistry.

(7) Little, R. D.; Brown, L. M.; Masjedizadeh, M. R. *J. Am. Chem. Soc.* **1992**, *114* (8), 3071.

(8) (a) Beckwith, A. L. J. *Chem. Soc. Rev.* **1993**, *22* (3), 143. (b) Gaudiano, G.; Koch, T. H. *Chem. Res. Tox.* **1991**, *4* (1), 2. (c) Nootens, C.; Merenyi, R.; Janousek, Z.; Viehe, H. G. *Bull. Soc. Chim. Belg.* **1988**, *97* (11−12), 1045. (d) Cossy, J.; Madaci, A.; Pete, J. P. *Tetrahedron Lett.* **1994**, *35* (10), 1541.

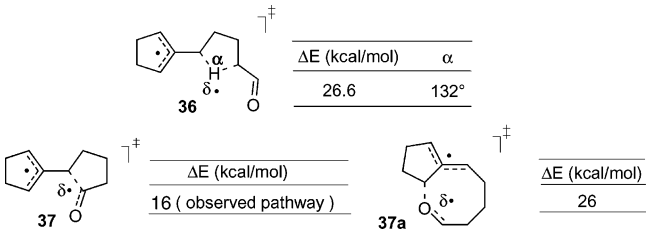
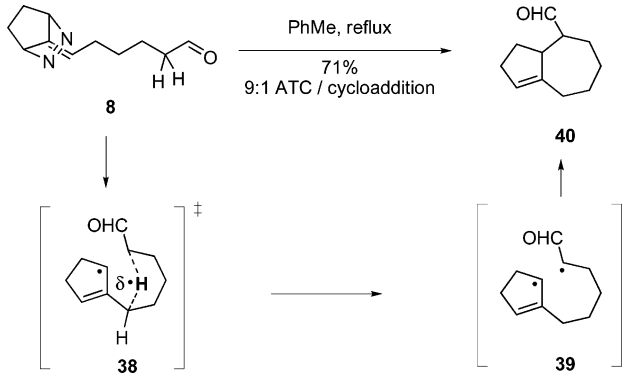


FIGURE 1. Comparison of energy differences between cycloaddition and atom transfer paths.

the energy surface.[9] Transition states for atom transfer and two cycloaddition paths were modeled, and the difference between the transition state energy and that of the starting triplet diyl, ΔE, were compared. As shown in Figure 1, a 5-exo-trig cyclization is preferred over the 8-endo-trig option, despite the fact that the latter affords an oxygen-stabilized radical (cf., **37** and **37a**). Gratifyingly, theory agrees with experiment, placing the cycloaddition pathway substantially below that for atom transfer. Notice, too, the comparatively small transfer angle, $\alpha = 132°$, a value that is apparently too small to accommodate atom transfer, for it is not observed.[2b,c,10]

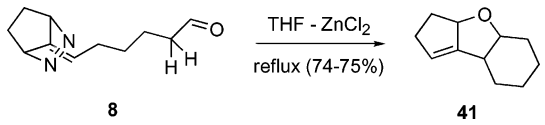
SCHEME 6



While **6** and **7** undergo cycloaddition exclusively, the addition of one more methylene unit between the diyl and site of transfer provides sufficient flexibility to attain the requisite geometry for atom transfer. Thus ATC constitutes the *preferred* reaction pathway in the chemistry of the diyl obtained from **8**. This is so despite the fact that the radical formed following atom transfer, **39**, is stabilized by just one substituent (viz., CHO). While previous reports from these laboratories suggested that two radical stabilizing groups were needed to achieve atom transfer, this is clearly not the case.[2a] To be fair, it is important to note that our previous studies placed either an α-hydroxy *ester* or an α-hydroxy *nitrile* at the end of the tether. In **8** a single *aldehyde* unit has replaced the two radical stabilizing groups. We wondered whether a single ester would work just as well. It does not. When CHO is replaced by CO_2Me, the resulting diyl dimerizes rather than engaging in either ATC or cycloaddition.

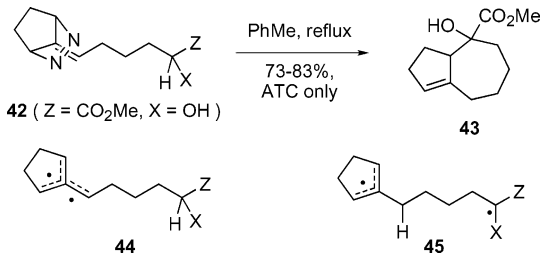
Like **5**, the presence of a Lewis acid changes the course of the chemistry. Thus, *no* atom transfer is observed when diazene aldehyde **8** is heated in refluxing THF containing zinc chloride. Instead, cycloaddition occurs to afford a mixture of diastereomeric products, **41**. It seems that the carbonyl π-bond has once again been weakened sufficiently to allow cycloaddition to occur, and this time, to also tip the scales entirely toward cycloaddition and away from ATC.

SCHEME 7



While not a prerequisite for atom transfer, the benefit of two radical stabilizing groups is evident in the contrasting chemistries of the diyls derived from diazenes **8** and **42**. Unlike **8**, where a mixture of ATC and cycloaddition is observed, only the ATC pathway is followed when a captodative radical is generated from diazene **42**. From these results we conclude that the *two most important factors in determining whether ATC will occur* are (1) the length of the tether and (2) the presence of one or more radical stabilizing groups at the site from which the hydrogen is being transferred.

SCHEME 8



It is interesting to compare the transition structures for the straight chain and captodative systems, **47** and **48**, respectively (see Figures 3 and 4). In so-doing we will use the three parameters defined in structure **46**: d_1, the distance between the hydrogen undergoing transfer and the carbon from which it is migrating, C_λ; d_2, the distance between the hydrogen being transferred and the carbon to which it is migrating, C_ϵ; and α, the angle C_λ–H–C_ϵ, referred to earlier in this paper as the transfer angle.

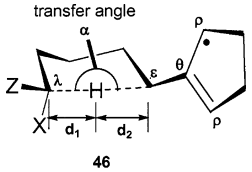
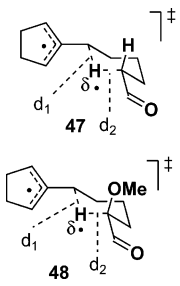


FIGURE 2. Important geometric parameters for atom transfer reactions.

(9) (a) Calculations were conducted with the Spartan 02 PC Software program available from Wavefunction, Inc. (b) Monoradicals and TMM diyls differ in several important ways. In particular, the latter can exist in more than one spin state (singlet/triplet) whose geometries (planar/bisected) and chemistries often differ, and second, because they are *di*radicals, there are two possible sites to which atom transfer can occur. That a 1,7-hydrogen transfer is not observed despite the fact that the transition state for it is calculated to reside only 1 kcal/mol above that for the 1,5 transfer is consistent with the notion that such a process is slowed entropically by the necessity to form an eight-membered ring in the transition structure leading to transfer.

(10) (a) Huang, X. L.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56* (18), 5421. (b) Curran, D. P.; Shen, W. J. *Am. Chem. Soc.* **1993**, *115* (14), 6051. (c) Schliesser, C. H.; Skidmore, M. A. Calculations: a Useful Tool for Synthetic Chemists. In *Radicals In Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: New York, 2001; Vol. 1, Chapter 3.2 and references therein.



transition structure	α	d_1 (Å)	d_2 (Å)
47	154°	1.347	1.379
48	151°	1.419	1.341

FIGURE 3. Comparison of atom transfer transition state geometries.

Quantum calculations (*U*B3LYP/6-31G*) of the transition structure for 1,5-hydrogen transfer within the triplet diyl of the straight chain aldehyde derived from **8** place the migrating atom approximately midway between the origin and terminus, though the length of the bond to the terminus, d_2, is somewhat shorter than that to the origin, d_1 (d_2 = 1.347 Å vs d_1 = 1.379 Å).[9b] Note, again, Figures 3 and 4. The C($\epsilon-\theta$) bond has lengthened from 1.413 Å in the starting structure to 1.464 Å in the transition structure (**47**), while the ring bonds have equalized (C($\theta-\rho$) = 1.405 Å) in consonance with the development of an allylic radical. Both centers, C_λ and C_ϵ, are distorted toward pyramidal. The geometry is reminiscent of that generally associated with γ-hydrogen atom transfer to the oxygen atom of a triplet carbonyl excited state in a Norrish Type II photoreaction.[11] Of particular note, and common to both systems, **47** and **48**, is the flattening of the ring that occurs to accommodate the large transfer angle (α ~ 154°),[10] some 20° greater than that calculated for transition structure **36**, a system for which atom transfer does not occur.

The transition structure for the captodative system, **48**, is enlightening. As shown in Figure 3, the hydrogen being transferred is much closer to the carbon from which it is migrating (d_1) than to the site where it will eventually reside (d_2). The migration has not advanced nearly as far in this system as it has in **47**. That is, the transition state occurs earlier along the reaction coordinate. This is consistent with the existence of a more exothermic process leading from the initial diyl to the captodatively stabilized distonic diyl, rather than to a system where the newly formed radical is stabilized only by the aldehyde unit.

As illustrated in Figure 4, calculations corroborate these suggestions. The captodatively stabilized triplet diyl **45** (Scheme 8, Z = CHO, X = OMe) is calculated to be ~11 kcal/mol *more* stable than the starting TMM diyl **44**, while the less stabilized diyl produced from **47** after atom transfer (viz., **39**, Z = CHO, X = H, Scheme 6) is 2 kcal/mol *less* stable than the TMM diyl from which it was produced.

In addition to providing useful insights concerning the hypersurface for these processes, the calculations have proven enlightening in other ways. For example, we previously hypothesized that the newly formed radical site in ATC reactions would be "close enough" to one of

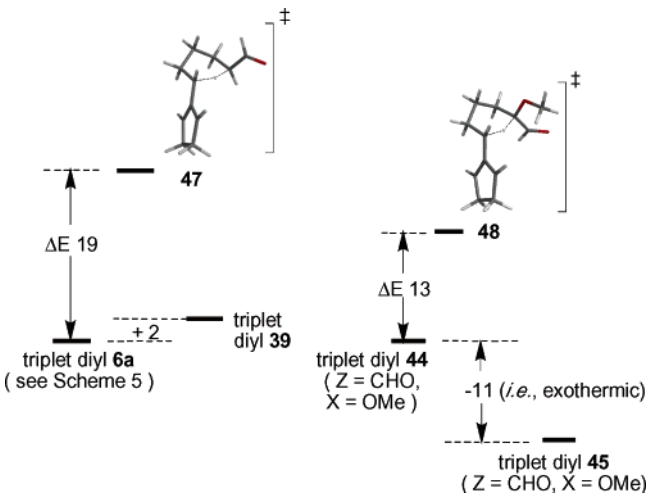
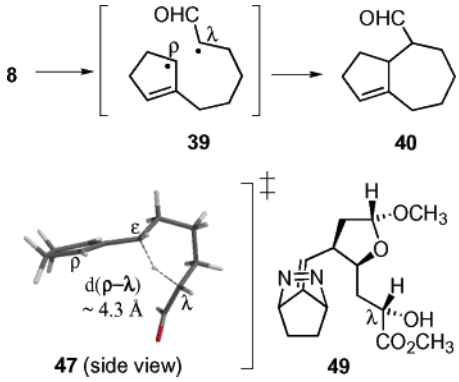


FIGURE 4. Early transition state leading to captodatively stabilized distonic diyl.

SCHEME 9



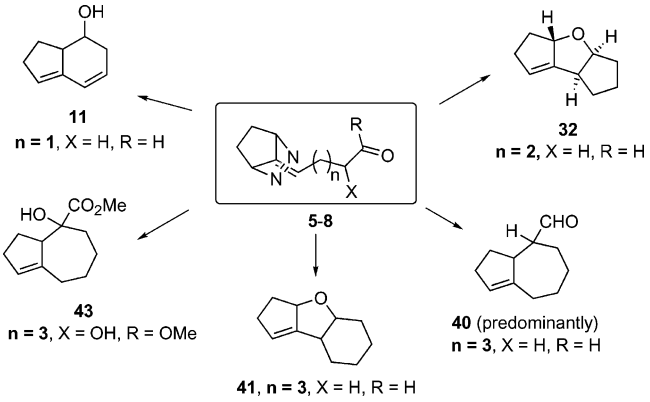
the odd electron centers located on the ring to allow σ-bond formation to occur immediately following the atom transfer event. For the transformation highlighted in Scheme 9, that bond would be between atoms C_ρ and C_λ of **39**. Of course, this begs the question: How fast is "immediately"? We do not know, though we do plan to examine this issue experimentally. At this point, calculations suggest that the event is not likely to be as fast as we initially projected. The shortest distance between the radical site being formed, C_λ, and either of the odd electron centers on the ring in transition structure **47** is calculated to be ~4.3 Å, a value that is certainly too large to accommodate our original hypothesis. This finding is consistent with our previous observation that the absolute configuration at C_λ is not retained in the ATC chemistry of the diyl derived from enantiomerically pure diazene **49**;[3] by the time the reactive centers close within bonding range, the radical has lost its configurational integrity.

Concluding Remarks

On the basis of the chemistry described in this paper we formulate the following guidelines: (1) In the absence of a Lewis acid, diyl dimerization will occur if the tether length is too short to allow it to attain the requisite geometry for atom transfer (viz., n = 1, Scheme 10). In the presence of a Lewis acid, however, the chemistry can

(11) (a) Dorigo, A. E.; McCarrick, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 4368. (b) Dorigo, A. E.; McCarrick, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 7508. (c) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7500.

SCHEME 10



be diverted in a useful manner even when the tether is short (e.g., **5** to **11**). (2) Cycloaddition will occur when a five-membered ring can be formed via addition to the carbonyl carbon of the acceptor aldehyde unit ($n = 2$, or when $n = 3$ in the presence of zinc chloride). (3) ATC predominates when the tether length is long enough to accommodate a "nearly linear" atom transfer angle, and is the sole reaction pathway when the radical center formed after transfer is captodatively stabilized. The two most important factors in determining whether ATC will occur are (1) the length of the tether and (2) the presence of one or more radical stabilizing groups at the site from which the hydrogen is being transferred.

We find it remarkable that such a wide range of structures can be obtained from such similar starting materials. Thus, by simply varying the length of the tether within diazenes **5**−**8**, one can selectively access any of the diverse skeletal types illustrated in Scheme 10. These results add considerably to the scope of TMM diyl chemistry. We hope that it will render the chemistry of greater utility to us and to others who might wish to explore it in greater detail, or to use it to help solve interesting problems.

Experimental Section

Calculations. Computations were conducted with Spartan '02 software, available from Wavefunction, Inc. The triplet ground state of each TMM diyl was minimized (planar geometry), then various atom transfer and cycloaddition transition states were found at the AM1 level of theory. The geometry was then re-optimized by using ab initio methods at the UHF/3-21G* level. Some geometries were further investigated with density functional theory and larger basis sets at the UB3LYP/6-31G* level. This procedure was followed to rapidly produce approximate geometries for further refinement and minimize the amount of time used in high-level computations. Unfortunately, the energies calculated by Hartree−Fock methods are inaccurate for H-atom transfers even though the geometry is close to that produced by DFT. On the basis of comparisons with computations done on monoradical H-atom transfers, we conclude that B3LYP/6-31G* is sufficiently accurate and is less expensive than higher level MP2/6-31G* calculations. Energies corresponding to the distonic diyl intermediates that result from the atom transfer process were determined for the triplet spin state.

Minima and transition state geometries were optimized without imposing constraints. When stationary points were identified, frequency calculations were performed. The minima were found to have no imaginary frequencies and the transition states each had one. The imaginary frequency of each transition state was analyzed and found to correspond to movement along the reaction coordinate.

Several reactant conformations were used as the initial geometry from which the transition state searches were begun at the AM1 level; those that produced the lowest energy transition states were investigated further at the B3LYP/6-31G* level of theory. As expected, a pseudoequatorial disposition of the substituents about the cycle corresponding to the cyclic transition state for atom transfer led to lower energies than alternative dispositions.

As in the case of intramolecular atom transfers of monoradicals, the tether length is a critical parameter in determining the energy difference between ground and transition states. Two possible sites for atom transfer to the diyl exist. One is to the exocyclic carbon, the other is to one of the endocyclic radical centers. Reaction between the diyl and the aldehyde π-system is also possible. These processes were investigated as well and some transition states were found. Both singlet and triplet diyls were investigated.

General Procedure A: Preparation of Fulvenes. To a solution of aldehyde (1.0 mmol) and cyclopentadiene (3.0 mmol) in MeOH (2.5 mL) at 0 °C was added pyrrolidine (1.5 mmol), dropwise via syringe. The resulting homogeneous mixture was allowed to warm to room temperature. After 5 h, the reaction mixture was cooled to 0 °C, and glacial acetic acid (4.5 mmol) was added dropwise. After 30 min the solution was diluted with water (2 mL), and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layers were washed with saturated $NaHCO_3$ (5 mL) and brine (5 mL), dried over magnesium sulfate, and concentrated in vacuo. Chromatography on silica gel (5−10% ether/pentane) afforded each of the fulvenes as a bright yellow oil.

General Procedure B: Diels−Alder Cycloaddition and Reduction of Δ (5,6) π-Bond. To a solution of fulvene (1.0 mmol) in methylene chloride (3.0 mL) was added diethyl azodicarboxylate (1.5 mmol) at 0 °C. The solution was stirred for 5−6 h at 0 °C and the progress was monitored by TLC and continued until the complete disappearance of the fulvene was noted. The solution was diluted with CH_2Cl_2 (5.0 mL), followed by the addition of dipotassium azodicarboxylate (8.0 mmol); the mixture was stirred with an overhead stirrer. The reaction mixture was cooled to 0 °C, and glacial acetic acid (9.0 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise via addition funnel. A vigorous gas evolution took place and the reaction mixture was stirred for 3−4 h after it ceased. The color of the TLC spots changed from black to blue as the reaction progressed, appearing at the same R_f as the starting material (vanillin stain). The solids were removed by filtration through a sintered glass funnel and were washed thoroughly with CH_2Cl_2. The solvent was washed with brine, dried, and removed under reduced pressure and the very viscous oil was purified by chromatography on silica gel (20% ether/pentane) to afford pure carbamate as a white foam.

General Procedure C: Preparation of Carbamate Alcohols (Scheme 2, Series 1). To a solution of carbamate (1.0 mmol) in THF (2.5 mL) was added tetrabutylammonium fluoride (1.5 mL of a 1 M solution in THF, 1.5 mmol) at 0 °C and the resulting solution was allowed to warm to room temperature. The mixture was stirred for another 1.5 h. Saturated NH_4Cl solution (1.5 mL) was added, and the reaction mixture was stirred for 5−10 min. It was then diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried, and evaporated under reduced pressure. The crude product was purified by flash chromatography; elution with ether afforded the carbamate alcohols **19b**, **20b**, and **21b** as colorless foams.

General Procedure D: Diazene Preparation. To a solution of carbamate (1.0 mmol) in ethanol (1.0 mL) and THF (0.25 mL) was added a solution of potassium hydroxide (8.0 mmol) in ethanol (2.5 mL) at room temperature. The resulting mixture was refluxed for 2.5 h and then cooled to room

temperature. Solvent was evaporated under reduced pressure. The reaction mixture was diluted with a mixture of DMSO (2.0 mL) and CH_2Cl_2 (1.0 mL) and cooled to 0 °C. Iodobenzene diacetate (3.0 mmol) was added to the solution and stirred for 2−3 h at the same temperature. A saturated solution of $NaHCO_3$ (5 mL) was added to the reaction mixture and stirred for another 5−10 min. The solids were removed by filtration through a sintered glass funnel and washed thoroughly with ether. The organic phase was separated and the aqueous phase was extracted several times with ether. Combined solvents were washed with brine, dried over sodium sulfate, and removed under reduced pressure and the resulting viscous oil was purified by chromatography on silica gel (100% ether) to afford pure diazene as a colorless oil.

General Procedure E: Preparation of Diazene Aldehyde (Scheme 2, Series 1). To a stirred solution of diazene alcohol (1.0 mmol) dissolved in a mixture of dry CH_2Cl_2 (1.6 mL) and DMSO (2.0 mL) at 0 °C was added triethylamine (5.0 mmol). After 2 min SO_3·Py complex (5.0 mmol) was added in one portion and the resulting mixture was stirred at 0 °C for 1 h. The reaction mixture was then quenched with water and extracted with ether and the organic layer was washed with brine and dried over Na_2SO_4. The combined ether solutions were removed under reduced pressure and the resulting oil was purified by chromatography on silica gel (100% ether) to afford pure diazene aldehydes (**5**−**8**) as colorless oils.

General Procedure F: Thermal Diyl Trapping Reaction and ATC in the Absence of Lewis Acid. A 1-L round-bottom flask was charged with toluene (500 mL) and degassed with argon for 1 h. A reflux condenser was then attached to the round-bottom flask. To the top of the reflux condenser was attached a syringe pump and the system was purged again with argon. The solution of diazene aldehyde (2.43 mmol) in previously degassed toluene (20 mL) was slowly added via syringe pump through the condenser into the refluxing toluene over 3 h; refluxing was continued for another 2 h. The solution was then cooled to room temperature, and the solvent was removed in vacuo. The crude oil was purified by chromatography on silica gel.

General Procedure G: Thermal Diyl Trapping Reaction in the Presence of a Lewis Acid. A solution of diazene aldehyde (1.0 mmol) and $ZnCl_2$ (2.5 mmol) in THF (100 mL) was placed in a 500-mL round-bottomed flask equipped with a reflux condenser and degassed by bubbling N_2 and Ar through the solution for 1 h. The solution was then refluxed for 3 h under N_2 and cooled to room temperature. The solvent was reduced to 50 mL in vacuo. The reaction mixture was quenched with water (20 mL) and the aqueous layer was extracted with ethyl acetate. The organic phase was washed with brine and dried over Na_2SO_4. Solvents were removed under reduced pressure and the colorless oil was purified by chromatography on silica gel.

General Procedure H: Photochemical Diyl Trapping Reaction. A mixture of diazene aldehyde (0.22 mmol) in acetonitrile (200 mL) was placed in a Pyrex round-bottomed flask, positioned 2−3 cm from the lamp, and degassed with argon for 30 min. A stirred solution of the sample was irradiated with a 450 W Hanovia lamp (water-cooled) for 2 h under a nitrogen atmosphere at room temperature. The solvent was removed in vacuo to obtain crude product, which was purified by chromatography on silica gel when needed.

5-[4-(*tert*-Butyldimethylsiloxy)butylidene]-1,3-cyclopentadiene (16; Scheme 2, Series 1, Step c). 4-*tert*-Butyldimethylsilyloxybutanal[12] (6.0 g, 29.7 mmol) was transformed into the fulvene **16** (6.5 g, 88%) as described in general procedure A. TLC R_f 0.6 (SiO_2, 20% ether/pentane), UV, vanillin; IR (neat) 2954, 2857, 1649, 1479, 1380, 1251, 1100, 842, 765, 727 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.55 (br d, J = 4.0 Hz, 2H, Cp H), 6.53−6.42 (m, 2H, Cp H), 6.21 (dt, J = 5.2, 1.6 Hz, 1H, C=C***H***), 3.68 (t, J = 6.4 Hz, 2H, C***H₂***OTBS), 2.59 (q, J = 7.6 Hz, 2H, C=CHC***H₂***), 1.76 (m, 2H, C***H₂***CH_2-OTBS), 0.92 (s, 9H, SiC(C***H₃***)₃), 0.069 (s, 3H, SiC***H₃***), 0.062 (s, 3H, SiC***H₃***); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.3, 142.8, 133.1, 130.9, 125.7, 119.3, 62.4, 32.7, 27.7, 26.1, 18.4, −5.1; LRCI-MS m/z 193 ($M^+ - C_4H_9$), 163, 117, 101, 92, 75, 59; HRMS calcd for ($C_{15}H_{26}OSi - C_4H_9$) 193.104869, found 193.104036.

Diethyl 7-[4-(*tert*-Butyldimethylsiloxy)butylidene]-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (Scheme 2, Series 1, Step d). Fulvene **16** (6.0 g, 24.0 mmol) was transformed into 8.4 g of pure carbamate according to the general procedure B in 84% yield. TLC R_f 0.35 (SiO_2, 20% ether/pentane), vanillin; IR (neat) 2932, 2860, 1742, 1704, 1462, 1371, 1309, 1250, 1186, 1096, 834, 796, 770 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.41−5.29 (br m, 1H, C=C***H***), 4.92−4.90 (m, 1H, NC***H***CH_2), 4.1−4.08 (br m, 5H, NC***H***CH_2, 2 × C***H₂***CH_3), 3.57−3.50 (m, 2H, C***H₂***OTBS), 2.14−2.02 (m, 2H, C=CHC***H₂***), 1.86−1.46 (m, 6H, C***H₂***CH_2OTBS, NCHC***H₂***C***H₂***-CHN), 1.28−1.21 (m, 6H, 2 × CH_2C***H₃***), 0.87−0.86 (br s, 9H, C(C***H₃***)₃), 0.026−0.019 (br s, 6H, Si(C***H₃***)₂). Due to the existence of a dynamic equilibrium between isomers at room temperature, the peaks are broad and few low-intensity peaks (equilibrating isomers) are also observed: ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.0, 157.1, 144.4, 117.1, 108.6, 62.6, 62.2, 60.4, 32.6, 26.0, 25.8, 25.0, 21.1, 18.3, 14.6, 14.3, −5.17, −5.19; LRCI-MS m/z 369 ($M^+ - C_4H_9$), 325, 251, 233, 221, 209, 193, 167, 149, 119, 103, 92, 75, 59; HRMS calcd for ($C_{21}H_{38}N_2O_5Si - C_4H_9$) 369.184576, found 369.183585.

Diethyl 7-(4-Hydroxybutylidene)-2,3-diazabicyclo[2.2.1]-heptane-2,3-dicarboxylate (19a; Scheme 2, Series 1, Step e). TBS protected carbamate (8.0 g, 18.8 mmol) was deprotected to give carbamate alcohol **19a** (5.2 g, 90%) as a colorless foam following general procedure C. TLC R_f 0.25 (SiO_2, 50% EtOAc/hexane), vanillin; IR (neat) 3500, 2935, 2859, 1709, 1465, 1400, 1374, 1311, 1187, 1149, 1104, 1059, 868, 837, 768 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.26 (br m, 1H, C=C***H***), 4.99−4.80 (m, 1H, NC***H***CH_2), 4.13−4.0 (br m, 5H, NC***H***CH_2, 2 × C***H₂***CH_3), 3.49−3.39 (m, 2H, C***H₂***OH), 2.61−2.37 (br s 1H, OH), 2.18−1.96 (m, 2H, C=CHC***H₂***), 1.96−1.46 (m, 6H, C***H₂***-CH_2OH, NCHC***H₂***C***H₂***CHN), 1.27−1.18 (m, 6H, 2 × CH_2C***H₃***). Due to the existence of a dynamic equilibrium between isomers at room temperature, the peaks are broad and few low-intensity peaks (equilibrating isomers) are also observed: ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.1, 157.5, 144.5, 138.7, 125.4, 116.9, 108.3, 62.6, 62.2, 60.8, 53.5, 31.9, 30.2, 29.6, 25.4, 24.8, 14.45, 14.42; ESI+/TOF m/z 335 (M^+ + Na); HRMS calcd for ($C_{15}H_{24}N_2O_5$ + Na) 335.15774, found 335.15771.

4-(2,3-Diazabicyclo[2.2.1]hept-2-en-7-yliden)-1-butanol (19b; Scheme 2, Series 1, Step f). Carbamate alcohol **19a** (5.0 g, 16.0 mmol) afforded 1.9 g of pure diazene alcohol as a colorless oil following general procedure D in 75% yield. TLC R_f 0.35 (SiO_2, 100% ether), vanillin; IR (neat) 3403, 2946, 1723, 1480, 1285, 1113, 1058, 908, 847, 808, 783, 772, 764, 757, 727 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.38 (app s with very small coupling, 1H, J = 2.0, NC***H***CH_2), 5.0 (overlapping t and d, J = 7.0, 2.8 Hz, 2H, C=C***H,*** NC***H***CH_2), 3.52 (t, J = 6.4 Hz, 2H, C***H₂***OH), 2.23−2.19 (br m, 1H, OH), 2.08−1.98 (m, 2H, C=CHC***H₂***), 1.65−1.61 (m, 2H, exo hydrogen on ethano bridge), 1.60−1.50 (m, 2H, C***H₂***CH_2OH), 1.06 (app d, 2H, J = 8.4 Hz, endo hydrogen on ethano bridge); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.2, 116.9, 76.9, 72.7, 61.6, 32.1, 25.3, 21.5, 21.1; ESI+/TOF m/z 355 ($2M^+$ + Na), 189 (M^+ + Na), 174, 167, 101; HRMS calcd for ($C_9H_{14}N_2O$ + Na) 189.09983, found 189.0998.

4-(2,3-Diazabicyclo[2.2.1]hept-2-en-7-yliden)butanal (5; Scheme 2, Series 1, Step b). Diazene alcohol **19b** (1.0 g, 6.0 mmol) gave 0.86 g of pure diazene aldehyde **5** as a colorless oil according to general procedure E in 87% yield. TLC R_f 0.52 (SiO_2, 100% ether), vanillin; IR (neat) 2947, 2868, 2730, 1720, 1479, 1439 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.69 (t, J = 1.2 Hz, 1H, C***H***O), 5.22 (app s with very small coupling, J = 1.1

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Hz, 1H, NC***H***CH_2), 5.05 (app t, J = 2.0 Hz, 1H, NC***H***CH_2), 5.04 (t, J = 7.8 Hz, 1H, C=C***H***), 2.45 (dt, J = 1.6, 7.8 Hz, 2H, C***H₂***CHO), 2.24 (m, 2H, C=CH***CH₂***), 1.62−1.58 (m, 2H, exo hydrogen on ethano bridge), 0.95 (app dt, J = 3.2, 7.6 Hz, 2H, endo hydrogen on ethano bridge); ^{13}C NMR (100 MHz) δ 201.1, 146.3, 115.2, 76.8, 72.6, 43.3, 21.7, 21.4, 20.9; LRCI-MS *m/z* 165 (M + 1), 153, 137, 119, 109, 93, 86, 80, 67, 55; HRMS calcd for ($C_9H_{12}N_2O$ + H) 165.102788, found 165.103129.

Bicyclo[4.3.0]nona-4,6-dien-2-ol (31; Scheme 4). Diazene aldehyde **5** (0.2 g, 1.2 mmol) afforded 0.12 g (73%) of pure alcohol **31** as a colorless oil following general procedure G. TLC R_f 0.56 (SiO_2, 20% EtOAc/hexane), vanillin; IR (neat) 3390, 3032, 2924, 1666, 1434, 1325, 1211, 1140, 1084, 1022, 991, 903, 862, 834, 722 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.35 (dd, J = 2.9, 6.7 Hz, 1H, CH=CCH=CH), 5.68 (d, J = 2.3 Hz, 1H, CH=CCH=CH), 5.61 (m, 1H, CH=CCH=CH), 4.01 (td, J = 2.1, 5.2 Hz, 1H, C***H***OH), 2.87 (m, 1H, C***H***CHOH), 2.53−2.29 (m, 4H), 2.00−1.80 (m, 2H); ^{13}C NMR (100 MHz) δ 137.0, 127.6, 125.1, 123.8, 66.1, 48.1, 34.7, 31.4, 24.7; LREI-MS *m/z* 136 (M^+), 117, 91, 79, 65, 41; HRMS calcd for $C_9H_{12}O$ 136.088815, found 136.089002.

5-[5-(*tert*-Butyldimethylsiloxy)pentylidene]-1,3-cyclopentadiene (17; Scheme 2, Series 1, Step c). 5-*tert*-Butyldimethylsilyloxypentanal[13] (5.0 g, 23.1 mmol) was transformed into fulvene **17** (5.42 g, 89%) as a yellow oil following general procedure A. TLC R_f 0.65 (SiO_2, 20% EtOAc/hexane), vanillin; IR (neat) 2928, 2857, 1648, 1471, 1380, 1255, 1095, 834, 764, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.57 (br d, J = 1.6 Hz, 2H, Cp H), 6.57−6.41 (m, 2H, Cp H), 6.22 (dt, J = 5.2, 1.6 Hz, 1H, C=C***H***), 3.68 (m, 2H, C***H₂***OTBS), 2.59 (q, J = 8.0 Hz, 2H, C=CHC***H₂***), 2.55−1.61 (2 m, 4H, C***H₂***C***H₂***CH_2-OTBS), 0.94 (s, 9H, SiC(C***H₃***)$_3$), 0.09 (s, 6H, Si(C***H₃***)$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.2, 143.0, 133.1, 130.8, 125.7, 119.2, 62.8, 32.5, 30.9, 26.1, 25.9, 18.5, −5.11, −5.13; LRCI-MS *m/z* 207 ($M^+ - C_4H_9$), 183, 147, 133, 115, 104, 91, 75, 59; HRMS calcd for ($C_{15}H_{26}OSi - C_4H_9$) 207.120519, found 207.120198.

Diethyl 7-[5-(*tert*-Butyldimethylsiloxy)pentylidene]-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (Scheme 2, Series 1, Step d). Carbamate (6.8 g, 82%) was prepared from fulvene **17** (5.0 g, 18.9 mmol) following general procedure B. TLC R_f 0.35 (SiO_2, 20% EtOAc/hexane), vanillin; IR (neat) 2934, 2857, 1749, 1705, 1463, 1372, 1310, 1248, 1186, 1104, 836, 773 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.25−5.23 (br m, 1H, C=C***H***), 4.84−4.82 (m, 1H, NC***H***CH_2), 4.23−4.0 (br m, 5H, NC***H***CH_2, 2 × C***H₂***CH_3), 3.50−3.49 (m, 2H, C***H₂***OTBS), 2.07−1.88 (m, 2H, C=CHC***H₂***), 1.87−1.11 (m, 12H, C***H₂***CH_2OTBS, NCHC***H₂***C***H₂***CHN, 2 × CH_2C***H₃***), 0.86−0.76 (br s, 9H, C(C***H₃***)$_3$), 0.08−0.01 (br s, 6H, Si(C***H₃***)$_2$). Due to the existence of a dynamic equilibrium between isomers at room temperature, the peaks are broad and few low intensity peaks (equilibrating isomers) are also observed; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 157.0, 144.1, 138.3, 129.0, 128.2, 125.3, 118.1, 108.1, 62.8, 62.6, 32.2, 28.5, 26.0, 18.3, 14.5, 14.2, −5.25; LRCI-MS *m/z* 383 ($M^+ - C_4H_9$), 339, 267, 233, 207, 189, 163, 147, 133, 117, 105, 91, 75, 61, 49; HRMS calcd for ($C_{22}H_{40}N_2O_5Si - C_4H_9$) 383.200226, found 383.199726.

Diethyl 7-(5-Hydroxypentylidene)-2,3-diazabicyclo-[2.2.1]heptane-2,3-dicarboxylate (20a; Scheme 2, Series 1, Step e). TBS-protected carbamate (6.5 g, 14.7 mmol) was deprotected by using tetrabutylammonium fluoride to give carbamate alcohol **20a** (4.4 g, 92%) according to general procedure C. TLC R_f 0.25 (SiO_2, 50% EtOAc/hexane), vanillin; IR (neat) 3487, 2937, 2861, 1706, 1464, 1402, 1373, 1319, 1186, 1148, 1104, 1057, 870, 766 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.11−4.99 (br m, 1H, C=C***H***), 4.67−4.57 (m, 1H, NC***H***CH_2), 4.01−3.75 (br m, 5H, NC***H***CH_2, 2 × C***H₂***CH_3), 3.33−3.18 (m, 2H, C***H₂***OH), 1.88−1.76 (m, 2H, C=CHC***H₂***), 1.76−0.89 (m, 14H, C***H₂***C***H₂***CH_2OH, NCHC***H₂***C***H₂***CHN, 2 × CH_2C***H₃***). Due to the existence of a dynamic equilibrium between isomers at room temperature, the peaks are broad and few low-intensity peaks (equilibrating isomers) are also observed; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.3, 156.5, 143.5, 137.6, 116.9, 107.1, 61.9, 61.5, 61.2, 56.9, 53.2, 31.2, 28.5, 27.8, 25.8, 25.1, 13.8; ESI+/TOF *m/z* 675 ($2M^+$ + Na), 349 (M^+ + Na); HRMS calcd for ($C_{16}H_{26}N_2O_5$ + Na) 349.17339, found 349.1724.

5-(2,3-Diazabicyclo[2.2.1]hept-2-en-7-yliden)-1-pentanol (20b; Scheme 2, Series 1, Step f). Carbamate alcohol **20a** (4.0 g, 12.3 mmol) was transformed into the diazene alcohol **20b** (1.87 g, 86%), obtained as yellow oil following general procedure D. TLC R_f 0.37 (SiO_2, 100% ether), vanillin; IR (neat) 3409, 2939, 2861, 1719, 1571, 1479, 1439, 1284, 1114, 1058, 929, 842, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.27 (app d, J = 2.0 Hz, 1H, NC***H***CH_2), 5.0 (overlapping t and d, J = 7.6, 2.1 Hz, 2H, C=C***H***, NC***H***CH_2), 3.52 (t, J = 6.4 Hz, 2H, C***H₂***OH), 1.91−1.84 (m, 2H, C=CH***CH₂***), 1.55−1.51 (m, 2H, exo hydrogen on ethano bridge), 1.39−1.30 (m, 2H, C***H₂***CH_2-OH), 1.29−1.24 (m, 2H, C***H₂***CH_2CH_2OH), 0.97 (app d, J = 8.8 Hz, 2H, endo hydrogen on ethano bridge); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.1, 117.3, 76.9, 72.7, 62.7, 32.1, 28.9, 25.7, 21.6, 21.2; ESI+/TOF *m/z* 383 ($2M^+$ + Na), 203 (M^+ + Na), 181 (M^+ + 1); HRMS calcd for ($C_{10}H_{16}N_2O$ + H) 181.13408, found 181.1334.

5-(2,3-Diazabicyclo[2.2.1]hept-2-en-7-yliden)pentanal (6; Scheme 2, Series 1, Step b). Doering oxidation of diazene alcohol (1.0 g, 5.5 mmol) to make diazene aldehyde **6** (0.89 g, 90%) was performed according to general procedure E. TLC R_f 0.47 (SiO_2, 100% ether), vanillin; IR (neat) 2942, 2865, 2722, 1721, 1479 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.58 (t, J = 1.6 Hz, 1H, C***H***O), 5.22 (app d, J = 2.0 Hz, 1H, NC***H***CH_2), 4.96 (app d, J = 2.0 Hz, 1H, NC***H***CH_2), 4.94 (t, J = 7.6 Hz, 1H, C=C***H***), 2.24 (dt, J = 1.6, 7.6 Hz, 2H, C***H₂***CHO), 1.88 (m, 2H, C=CH***CH₂***), 1.54−1.47 (m, 4H, C***H₂***CH_2CHO, and exo hydrogen on ethano bridge), 0.95 (app dt, J = 2.0, 11.0, 2H, endo hydrogen on ethano bridge); ^{13}C NMR (100 MHz) δ 201.8, 145.7, 116.0, 76.5, 72.3, 42.6, 27.9, 21.4, 21.2, 20.8; LRCI-MS *m/z* 179 (M^+ + H), 151, 144, 133, 121, 107, 91, 83, 67, 57, 49; ESI-TOF *m/z* 201 (M^+ + Na), 193, 186, 179 (M^+ + H); HRMS calcd for $C_{10}H_{14}N_2ONa$ 201.09983, found 201.0996.

1,2,3,3a,4a,5,6,7b-Octahydrodicyclopenta[*b*,*d*]furan (32; Scheme 5). Diazene aldehyde **6** was subjected to deazetation under each of the three different diyl trapping reaction conditions described earlier as general procedures F, G, and H. The major product isolated by column chromatography from all three methods has identical spectral properties. Yield: general procedure F, 65%; General procedure G, 70%; general procedure H, 77−78%. TLC R_f 0.6 (SiO_2, 10% EtOAc/hexane), vanillin; IR (neat) 2931, 2853, 1445, 1329, 1148, 1057, 1045, 972, 953, 889, 853, 796, 761 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.50 (m, 1H, C=C***H***), 4.93 (m, 1H, HC=CC***H***), 4.85 (m, 1H, OC***H***CHC=C), 2.99 (ddd, J = 5.6, 8.0, 9.2 Hz, 1H, OCHC***H***C=C), 2.26−2.41 (m, 2H), 2.25 (m, 1H), 1.89−1.51 (m, 7H); ^{13}C NMR (100 MHz) δ 152.5, 120.7, 90.5, 88.4, 41.8, 35.9, 53.8, 34.2, 32.0, 26.3; LREI-MS *m/z* 150 (M^+), 135, 131, 121, 117, 106, 93, 91, 83, 79, 67, 53, 43; HRMS calcd for $C_{10}H_{14}O$ 150.104465, found 150.104334.

5-[6-(*tert*-Butyldiphenylsiloxy)hexylidene]-1,3-cyclopentadiene (18; Scheme 2, Series 1, Step c). 6-(*tert*-Butyldiphenylsilyloxy)hexanal[14] (6.0 g, 16.9 mmol) was transformed into fulvene **18** (6.1 g, 90%), obtained as a yellow oil following general procedure A. TLC R_f 0.68 (SiO_2, 20% EtOAc/hexane), UV, vanillin; IR (neat) 2930, 2857, 1649, 1476, 1380, 1252, 1109, 838, 765, 728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70−7.68 (m, 4H, ArH), 7.46−7.38 (m, 6H, ArH), 6.55−6.39 (m, 4H, Cp H), 6.22 (dt, J = 5.2, 1.7 Hz, 1H, C=C***H***), 3.67 (t, J = 6.3 Hz, 2H, C***H₂***OTBDPS), 2.53 (q, J = 7.2 Hz, 2H, C=CHC***H₂***), 1.65−1.42 (m, 6H, C***H₂***C***H₂***C***H₂***CH_2OTBDPS), 1.03 (s, 6H, Si(C***H₃***)$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 135.7, 134.2, 133.1, 130.8, 129.7, 127.7, 125.7, 119.3, 63.9, 32.5, 31.1, 29.3, 27.0, 25.7, 19.4.

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Diethyl 7-[6-(*tert*-Butyldiphenylsiloxy)hexylidene]-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (Scheme 2, Series 1, Step d). Carbamate (6.8 g, 79%) was prepared from fulvene **18** (6.0 g, 14.9 mmol) according to general procedure B. TLC R_f 0.21 (SiO_2, 20% EtOAc/hexane), vanillin; IR (neat) 2933, 2857, 1746, 1703, 1462, 1428, 1372, 1312, 1186, 1109, 867, 771 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.68−7.64 (m, 4H, ArH), 7.45−7.35 (m, 6H, ArH), 5.30−5.29 (br m, 1H, C=C***H***), 4.91−4.87 (m, 1H, NC***H***CH_2), 4.25−4.17 (br m, 5H, NC***H***CH_2, 2 × C***H₂***CH_3), 3.66−3.61 (m, 2H, C***H₂***OTBDPS), 2.08−2.02 (m, 2H, C=CHC***H₂***), 2.01−1.18 (m, 16H, C***H₂***C***H₂***-C***H₂***CH_2OTBDPS, NCHC***H₂***C***H₂***CHN, 2 × CH_2C***H₃***), 1.06−1.03 (br s, 9H, C(C***H₃***)$_3$). Due to the existence of a dynamic equilibrium between isomers at room temperature, the peaks are broad and few low-intensity peaks (equilibrating isomers) are also observed: ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.2, 144.0, 138.2, 135.7, 134.2, 129.7, 127.7, 63.9, 62.8, 62.7, 53.6, 32.5, 29.5, 28.9, 27.0, 25.5, 25.4, 19.3, 14.6; ESI+/TOF *m/z* 601 (M^+ + Na); HRMS calcd for ($C_{33}H_{46}N_2O_5Si$ + Na) 601.30682, found 601.3063.

Diethyl 7-(6-Hydroxyhexylidene)-2,3-diazabicyclo[2.2.1]-heptane-2,3-dicarboxylate (21a; Scheme 2, Series 1, Step e). TBDPS protected carbamate (6.5 g, 11.2 mmol) was deprotected to give carbamate alcohol **21a** (3.5 g, 94%) according to general procedure C. TLC R_f 0.23 (SiO_2, 50% EtOAc/hexane), vanillin; IR (neat) 3472, 2935, 2858, 1710, 1464, 1400, 1374, 1316, 1245, 1188, 1148, 1106, 1057, 864, 770, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.28−5.20 (br m, 1H, C=C***H***), 4.85−4.79 (m, 1H, NC***H***CH_2), 4.20−4.00 (br m, 5H, NC***H***CH_2, 2 × C***H₂***CH_3), 3.54−3.47 (m, 2H, C***H₂***OH), 2.36−2.27 (m, 3H, C=CHC***H₂***, OH), 2.03−1.89 (m, 16H, C***H₂***C***H₂***C***H₂***CH_2OH, NCHC***H₂***C***H₂***CHN, 2 × CH_2C***H₃***). Due to the existence of a dynamic equilibrium between isomers at room temperature, the peaks are broad and few low-intensity peaks (equilibrating isomers) are also observed; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 157.5, 144.0, 138.2, 117.4, 109.4, 62.4, 62.1, 60.4, 58.9, 32.4, 29.3, 28.6, 25.17, 25.10, 14.4, 14.1; ESI+/TOF *m/z* 363 (M^+ + Na); HRMS calcd for ($C_{17}H_{28}N_2O_5$ + Na) 363.18904, found 363.1885.

6-(2,3-Diazabicyclo[2.2.1]hept-2-en-7-yliden)-1-hexanol (21b; Scheme 2, Series 1, Step f). Carbamate alcohol **21a** (3.4 g, 10.0 mmol) was transformed into diazene alcohol **21b** (1.67 g, 86%) following general procedure D. TLC R_f 0.20 (SiO_2, 100% ether), vanillin; IR (neat) 3398, 2933, 2857, 1643, 1480, 1439, 1282, 1114, 1052, 894, 854, 845, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.39 (app d, J = 2.0 Hz, 1H, NC***H***CH_2), 5.11 (overlapping t and d, J = 7.6, 2.1 Hz, 2H, C=C***H***, NC***H***CH_2), 3.63 (dt, J = 2.0, 6.5 Hz, 2H, C***H₂***OH), 2.01 (br s, 1H, OH), 2.01−1.88 (m, 2H, C=CH***CH₂***), 1.68−1.51 (m, 2H, exo hydrogen on ethano bridge), 1.58−1.21 (m, 6H, C***H₂***C***H₂***C***H₂***-CH_2OH), 1.06 (app d, J = 8.8 Hz, 2H, endo hydrogen on ethano bridge); ^{13}C NMR (100 MHz) δ 146.9, 117.5, 72.8, 62.9, 55.2, 32.6, 29.3, 29.1, 25.3, 21.7, 21.2; ESI+/TOF *m/z* 411 ($2M^+$ + Na), 389 ($2M^+$ + H), 217 (M^+ + Na), 195 (M^+ + H), 167, 144; HRMS calcd for ($C_{11}H_{18}N_2O$ + Na) 217.13113, found 217.1313.

6-(2,3-Diazabicyclo[2.2.1]hept-2-en-7-yliden)hexanal (8; Scheme 2, Series 1, Step b). Doering oxidation of diazene alcohol **21b** (1.0 g, 5.1 mmol) to make diazene aldehyde **8** (0.89 g, 90%) was performed according to general procedure E. TLC R_f 0.45 (SiO_2, 100% ether), vanillin; IR (neat) 2940, 2860, 2722, 1719, 1479, 1441, 1390, 1284, 1113, 1085, 1041, 893, 847, 675 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.70 (t, J = 0.8 Hz, 1H, C***H***O), 5.33 (app d, J = 1.2 Hz, 1H, NC***H***CH_2), 5.07−5.03 (m, 2H, NC***H***CH_2, and C=C***H***), 2.38 (dt, J = 0.8, 7.2 Hz, 2H, C***H₂***CHO), 1.96 (m, 2H, C=CH***CH₂***), 1.61−1.49 (m, 4H, C***H₂***CH_2CHO, and exo hydrogen on ethano bridge), 1.35−1.27 (m, 2H, C***H₂***CH_2CH_2CHO), 0.95 (app d, J = 10.8 Hz, 2H, endo hydrogen on ethano bridge); ^{13}C NMR (100 MHz) δ 202.4, 145.3, 116.8, 76.9, 72.6, 43.6, 28.9, 28.8, 21.5, 21.4, 21.1; LRCI-MS *m/z* 193 (M^+ + H), 165, 147, 135, 125, 120, 109, 97, 81, 67; HRMS calcd for ($C_{11}H_{16}N_2O$ + H) 193.134088, found 193.134184.

Bicyclo[5.3.0]dec-7-ene-2-carbaldehyde (40) and 3,3a,4a,5,6,7,8,8aOctahydro-2*H*-benzo[*b*]cyclopenta[*d*]furan (41; Scheme 7). Under the conditions described in general procedure F, aldehyde **8** produced both **40** and **41** in a 9:1 ratio in a total yield of 72−73%. With use of general procedure G, aldehyde **8** produced only **41** in 74−75% yield. **40**: TLC R_f 0.60 (SiO_2, 10% EtOAc/hexane), vanillin; IR (neat) 2924, 2851, 2706, 1725, 1445, 1002, 795, 684, 653 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.73 (d, J = 0.8 Hz, 1H, C***H***O), 5.46 (m, 1H, C=C***H***), 3.25 (m, 1H, C=CC***H***), 2.96−2.83 (m, 1H, C***H***CHO), 2.67−1.21 (m, 12H); ^{13}C NMR (100 MHz) δ 204.8, 148.1, 126.3 (126.1), 56.7 (55.32), 47.2 (47.0), 31.7 (31.4), 31.2 (30.9), 30.15 (30.10), 28.8 (28.9), 27.6 (27.5), 23.5; LREI-MS *m/z* 164 (M^+), 146, 133, 122, 117, 105, 91, 79, 67, 53, 41; HRMS calcd for $C_{11}H_{16}O$ 164.120115, found 164.120600. **41**: TLC R_f 0.59 (SiO_2, 10% EtOAc/hexane), vanillin; IR (neat) 2929, 1695, 1047, 919, 877, 848, 798, 737, 722, 711, 691, 666 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.53 (dd, J = 1.6, 3.2 Hz, 1H, C=C***H***), 5.08 (m, 1H, C=CC***H***), 4.08 (m, 1H, OC***H***CHC=C), 2.52−2.35 (m, 3H, allylic), 2.33−2.26 (m, 1H), 2.04−1.97 (m, 1H), 1.72−1.65 (m, 2H), 1.64−1.60 (m, 1H), 1.59−1.42 (m, 3H), 1.32−1.09 (m, 2H); ^{13}C NMR (100 MHz) δ 153.3, 120.7, 86.59, 80.0, 39.0, 35.6, 33.8, 29.0, 26.0, 24.0, 20.1; LREI-MS *m/z* 164 (M^+), 146, 136, 131, 121, 107, 93, 83, 77, 67, 53, 41; HRMS calcd for $C_{11}H_{16}O$ 164.120115, found 164.120164.

1-(2,4-Cyclopentadienyliden)-3-[2-(4-methoxyphenyl)-(4*R*)-1,3-dioxolan-4-yl]propane (23; Scheme 2, Series 2, Step a). Fulvene **23** (5.45 g, 91%) was prepared from aldehyde **22**[15] (5.0 g, 21.1 mmol) according to general procedure A. TLC R_f 0.51 (SiO_2, 20% EtOAc/hexane), vanillin; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.44−7.35 (m, 2H, ArH), 6.93−6.87 (m, 2H, ArH), 6.59−6.38 (m, 4H, CpH), 6.20 (dt, J = 5.0, 1.6 Hz, 1H, C=C***H***), 5.76 (s, 1H, OC***H***O), 4.32−4.21 (m, 2H, OC***H***HC***H***O), 3.82 (s, 3H, OCH_3), 3.66−3.60 (m, 1H, OCH***H***CHO), 2.79−2.61 (m, 2H, C=CHC***H₂***), 2.02−1.72 (m, 2H, CH_2C***H₂***CO); ^{13}C NMR (100 MHz) δ 160.7, 141.3, 133.6, 131.1, 128.2, 128.0, 125.7, 119.2, 113.96, 113.94, 104.2, 76.3, 70.0, 55.5, 33.6, 27.6; LREI-MS *m/z* 284 (M^+), 179, 153, 135, 132, 117, 105, 92, 77, 65, 51, 43; HRMS calcd for $C_{18}H_{20}O_3$ 284.14124, found 284.14114.

Diethyl 7-3-[2-(4-Methoxyphenyl)-(4*R*)-1,3-dioxolan-4-yl]propylidene-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (Scheme 2, Series 2, Step b). Fulvene **23** (5.4 g, 19.0 mmol) was transformed into the carbamate (7.25 g, yellow foam, 83%) as described in general procedure B. TLC R_f 0.25 (SiO_2, 25% EtOAc/hexane), vanillin; IR (neat) 2980, 2938, 1742, 1702, 1615, 1588, 1516, 1373, 1306, 1247, 1187, 1105, 1030, 834, 773 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.41−7.34 (m, 2H, ArH), 6.92−6.86 (m, 2H, ArH), 5.73 (s, 1H, OC***H***O), 5.24 (br m, 1H, C=C***H***), 4.92 (m, 1H, NC***H***CH_2), 4.25−4.12 (m, 7H, NC***H***CH_2, C***H₂***(O), 2 X C***H₂***CH_3), 3.80 (s. 3H, OC***H₃***), 3.60 (m, 1H, CH_2C***H***(O)), 2.33−2.11 (m, 2H, C=CHC***H₂***), 1.97−1.48 (m, 6H, C=CHCH_2C***H₂***, NCHC***H₂***C***H₂***CHN) ,1.33−1.20 (m, 6H, 2 × CH_2C***H₃***). Due to the existence of a dynamic equilibrium between isomers at room temperature, the peaks are broad and few low-intensity peaks (equilibrating isomers) are also observed: ESI+/TOF *m/z* 943 ($2M^+$ + Na), 483 (M^+ + Na), 461 (M^+ + H), 325, 306, 270, 198; HRMS calcd for ($C_{24}H_{32}N_2O_7$ + Na) 483.2117, found 483.21107.

7-3-[2-(4-Methoxyphenyl)-(4*R*)-1,3-dioxolan-4-yl]propylidene-2,3-diazabicyclo[2.2.1]hept-2-ene (Scheme 2, Series 2, Step c). Carbamate (7.1 g, 15.4 mmol) prepared as described above was transformed into the diazene (3.92 g, yellow oil, 81%) following general procedure D. TLC R_f 0.54 (SiO_2, 100% ether), vanillin; IR (neat) 2941, 2887, 1614, 1517, 1303, 1248, 1170, 1079, 1034, 892, 830, 768, 735, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.40−7.30 (m, 2H, ArH), 6.91−6.82 (m, 2H, ArH), 5.65 (s, 1H, OC***H***O), 5.36 (app d, J = 3.0 Hz, 1H, NC***H***CH_2), 5.01 (br m, 2H, C=C***H***, NC***H***CH_2), 4.11−3.94 (m, 2H, CHC***H₂***O), 3.74 (s, 3H, OC***H₃***), 3.60 (m, 1H,

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CH_2CHO), 2.18−2.04 (m, 2H, C=CHC***H₂***), 1.72−1.51 (m, 4H, exo hydrogen on ethano bridge, C=$CHCH_2C$***H₂***), 1.03 (app d, 2H, J = 8.7 Hz, endo hydrogen on ethano bridge); ^{13}C NMR (100 MHz) δ 160.2 (160.1), 145.5 (145.4), 129.7 (130.2), 127.8 (127.7), 116.0, 113.5, 103.8 (102.8), 76.6, 75.8 (75.7), 72.4, 70.3 (69.73), 55.1, 33.1 (32.7), 25.4, 25.29 (25.25), 21.3 (20.8); ESI+/TOF *m/z* 337 (M^+ + Na), 309, 223; HRMS calcd for ($C_{18}H_{22}N_2O_3$ + Na) 337.1528, found 337.1521.

5-(2,3-Diazabicyclo[2.2.1]hept-2-en-7-yliden)-2-(4-methoxybenzyloxy)-(2*R*)-pentan-1-ol (Scheme 2, Series 2, Step d). To a stirred solution of the diazene (1.0 g, 3.18 mmol), whose preparation was just described, in CH_2Cl_2 (15 mL) was added Dibal-H (4.8 mL, 1.0 M solution in hexane, 4.8 mmol) at −78 °C. After 1 h, the reaction mixture was quenched with a dropwise addition of Rochelle's salt (20 mL), warmed to room temperature, and stirred for another 30 min. Then the mixture was extracted with CH_2Cl_2, and the organic phase was concentrated under reduced pressure and purified by silica gel column chromatography to give diazene alcohol (0.74 g, 74%) as a colorless oil. TLC R_f 0.35 (SiO_2, 100% ether), vanillin; IR (neat) 3425, 2942, 2865, 1612, 1586, 1513, 1455, 1348, 1301, 1248, 1176, 1033, 826, 752, 713 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26−7.19 (m, 2H, ArH), 6.87−6.82 (m, 2H, ArH), 5.32 (app s, 1H, NC***H***CH_2), 5.06−4.99 (br m, 2H, C=C***H***, NC***H***CH_2), 4.43, (q, J = 11.3 Hz, 2H, C***H₂***Ar), 3.75 (s, 3H, OC***H₃***), 3.63−3.31 (m, 3H, CH_2C***H***OPMB, C***H₂***OH), 2.57 (br s, 1H, OH), 2.08−1.89 (m, 2H, C=CHC***H₂***), 1.64−1.39 (m, 4H, exo hydrogen on ethano bridge, C=$CHCH_2C$***H₂***), 1.03 (app d, J = 8.2 Hz, 2H, endo hydrogen on ethano bridge); ^{13}C NMR (100 MHz) δ 159.8, 145.5, 130.3, 129.3, 116.9, 113.8, 78.5, 76.7, 72.5, 71.1, 63.7, 55.2, 30.8, 24.9, 21.4, 20.9; ESI+/TOF *m/z* 339 (M^+ + Na), 311, 146; HRMS calcd for ($C_{18}H_{24}N_2O_3$ + Na) 339.1685, found 339.1678.

5-(2,3-Diazabicyclo[2.2.1]hept-2-en-7-yliden)-2-(4-methoxybenzyloxy)-(2*R*)-pentanal (7; Scheme 2, Series 2, Step e). Doering oxidation of diazene alcohol (1.0 g, 5.5 mmol) to make diazene aldehyde **7** (0.89 g, 90%) was performed according to general procedure E. TLC R_f 0.5 (SiO_2, 100% ether), vanillin; IR (neat) 2944, 2863, 1729, 1612, 1512, 1455, 1302, 1247, 1175, 1111, 1031, 823, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.56 (d, J = 0.4 Hz, 1H, C*H*O), 7.25 (m, 2H, ArH), 6.90 (m, 2H, ArH), 5.34 (app s, 1H, NC***H***CH_2), 5.10−4.98 (m, 2H, NC***H***CH_2, and C=C***H***), 4.59−4.42 (m, 2H, CH_2OPMB), 3.79 (s, 3H, OCH_3), 3.68−3.60 (m, 1H, C***H***CHO), 2.16−1.95 (m, 2H, C=CHC***H₂***), 1.70−1.53 (m, 4H, exo hydrogen on ethano bridge, C=$CHCH_2C$***H₂***), 1.10−1.04 (app d, J = 8.2 Hz, 2H, endo hydrogen on ethano bridge); ^{13}C NMR (100 MHz) δ 203.9, 159.7, 146.1, 146.5, 129.8, 116.2, 114.1, 82.4, 76.9, 72.7, 55.4, 29.8, 22.8, 21.5, 21.1; ESI+/TOF *m/z* 629 ($2M^+$ + H), 315 (M^+ + H), 287, 189, 121; HRMS calcd for ($C_{18}H_{22}N_2O_3$ + H) 315.17031, found 315.1692.

5-(4-Methoxybenzyloxy)-(2*R*,5*S*,6*R*,8*R*)-tricyclo[6.3.0.0^{2,6}]-undec-1(11)-ene (33; Scheme 5). Diazene aldehyde **7** (350 mg, 1.1 mmol) was subjected to deazetation as described in general procedure F to afford the tricyclic heterocycle **33** (230 mg, 72%) as a colorless oil. TLC R_f 0.55 (SiO_2, 20% EtOAc/hexane), vanillin; IR (neat) 2936, 2854, 1698, 1612, 1512, 1462, 1301, 1247, 1172, 1071, 1039, 956, 817 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 (d, J = 8.0 Hz, 2H, aromatic), 6.87 (d, J = 8.0 Hz, 2H, ArH), 5.50 (m, 1H, C=C***H***), 4.89 (ddd, J = 0.8, 2.0, 8.0 Hz, 1H, HC=CC***H***), 4.74 (dd, J = 1.6, 6.4 Hz, 1H, OC***H***CHC=C), 4.51 (2d, J = 11.6 Hz, 2H, C***H₂***Ar), 3.93 (ddd, J = 2.4, 5.0, 8.0 Hz, 1H, C***H***OCH_2Ar), 3.79 (s, 3H, OCH_3), 3.17 (ddd, J = 4.0, 8.0, 12.0 Hz, 1H, OCHC***H***C=C), 2.56 (m, 2H, CHC=CHC***H₂***), 2.27 (m, 1H, OCHC***H***HCH_2), 2.08 (m, 1H, $ArCH_2OCHCH_2C$***H***H), 1.84 (m, 1H, $ArCH_2OCHC$***H***H), 1.77 (m, 1H, $ArCH_2OCHCH$***H***), 1.65 (m, 1H, OCHCH***H***CH_2), 1.50 (m, $ArCH_2OCHCH_2CH$***H***); ^{13}C NMR (100 MHz) δ 159.2, 151.3, 130.7, 129.4, 121.5, 113.9, 93.7, 88.2, 85.5, 70.9, 55.4, 40.4, 36.0, 33.9, 31.6, 28.9; LREI-MS *m/z* 286 (M^+), 165, 137, 121, 91, 77, 51; HRMS calcd for $C_{18}H_{22}O_3$ 286.157895, found 286.158011.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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