

of ring strain is widely accepted and correct, but it does not explain the full amount of the acceleration in the cyclic species.⁴ In particular, it appears that the acyclic transition states used as standards are destabilized compared to the corresponding cyclic cases. Although the rate enhancement in cyclic phosphates and phosphonates is the same, their strain energy is not the same. Our results suggest that the degree to which the cyclic esters are strained depends upon the number of oxygens in the ring. Further

work is necessary to establish the source of the higher energy of the acyclic transition states, but it appears reasonable that the crowding should be a serious problem in a five-coordinate species.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for continued support through an operating grant (R.K.) and a postgraduate fellowship (S.D.T.).

Expression of Dipolar Character in Diyl Trapping Chemistry

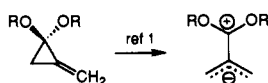
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Abstract: A set of new reactions is described and illustrated in eqs 1-5. Diazenes which customarily participate in diradical processes, compounds **1a** and **9** for example, lead to intermediates which are intercepted by water. Diazene **3** is converted to an intermediate which is intercepted both by water and, when the dielectric constant of the medium is sufficiently high, by *n*-PrOH. The chemistry is believed to arise through the intermediacy of a "dipolar diradical", which is described by an unequal weighting of the zwitterionic (Ψ_α and Ψ_β) and diradical (Ψ_δ) resonance formulations to the overall wave function for the system: $\Psi = \alpha\Psi_\alpha + \beta\Psi_\beta + \delta\Psi_\delta$.

Introduction

Recently, Nakamura reported a new [3 + 2] cycloaddition leading to the facile construction of functionalized five-membered-ring carbocycles.¹ The process is initiated thermally and occurs between 2-methylenecyclopropanone ketals and electron-deficient alkenes. It has been suggested, and the existing data is supportive, that a dipolar synthetic equivalent of the corresponding trimethylenemethane diradical is an intermediate. Particularly good evidence stems from the fact that the intermediate can be intercepted by methanol. The direction of the polarization with the positive charge being localized on the ketal-bearing carbon is certainly reasonable; molecular orbital (MO) calculations also support this view.¹



The diradicals which are commonly associated with the inter- and intramolecular diyl trapping reactions, in contrast, express dipolar character only in so far as they are intercepted most rapidly by electron-deficient diylphiles.² There is a substantial body of evidence, including the direct observation of triplet diradicals by ESR for a wide range of substituents R and R' in the formulation shown, to support a diradical rather than a zwitterionic intermediate.³ In keeping with this suggestion is the result of

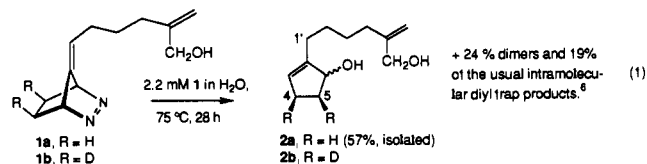


MO calculations which place the difference in energy between the highest energy singlet and the zwitterionic state of the parent

trimethylenemethane at greater than 4 eV.^{4,5}

A New Reaction. We report a series of new reactions which we believe can best be explained as proceeding through the intermediacy of a dipolar diyl. The wave function for this state can qualitatively be described as a linear combination of dipolar and diradical contributions, with the dipolar portion of sufficient magnitude to govern the mode of reactivity (*vide infra*).^{1b,5}

In conjunction with another project, we heated diazene **1a** to 75 °C in water.⁶ We thought that the hydrophobic diyl would undergo intramolecular diyl trapping in a manner which would lead to a different regio- and stereochemical outcome than we had previously observed when the diyl was generated in acetonitrile or THF. The usual diyl trapping products were obtained,⁶ but in diminished yield, while the isomer ratio was basically unchanged. We were surprised to notice the presence of a new compound, diol **2a**, a product which clearly resulted from the interception of an intermediate by water!⁷



(4) (a) Davis, J. H.; Goddard, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 303. (b) Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 2906. (c) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1977**, *99*, 2053. (d) Hood, D. M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 8009. (e) Dixon, D. A.; Foster, R.; Halgren, T. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 1359.

(5) Trimethylenemethane is a nondisjoint hydrocarbon and as such, no molecular orbitals exist where the two electrons in question can be located entirely on different atoms. Consequently, even for this simple system, the lowest energy singlet wave function contains ionic terms. As stated by Borden and Salem (*J. Am. Chem. Soc.* **1973**, *95*, 932): "The large ionic component in the singlet wave function for planar trimethylenemethane is responsible for its high energy". For an excellent account of the covalent vs zwitterionic character of the wave functions for diradicals, see: (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) *Electrons in Chemical Reactions - First Principles*; Salem, L., Ed.; Wiley: New York, 1982; pp 89-93.

(6) Masjedizadeh, M. R.; Dannecker-Doerig, I.; Little, R. D. *J. Org. Chem.* **1990**, *55*, 2742.

(1) (a) Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1989**, *111*, 7285. (b) Nakamura, E.; Yamago, S.; Ejiri, S.; Dorigo, A. E.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 3183.

(2) Little, R. D. *Chem. Rev.* **1986**, *86*, 875 and references therein. McLoughlin, J. I.; Brahma, R.; Campopiano, O.; Little, R. D. *Tetrahedron Lett.* **1990**, *31*, 1377.

(3) Masjedizadeh, M. R.; Fite, C.; Little, R. D. *Tetrahedron Lett.* **1990**, *31*, 1229.

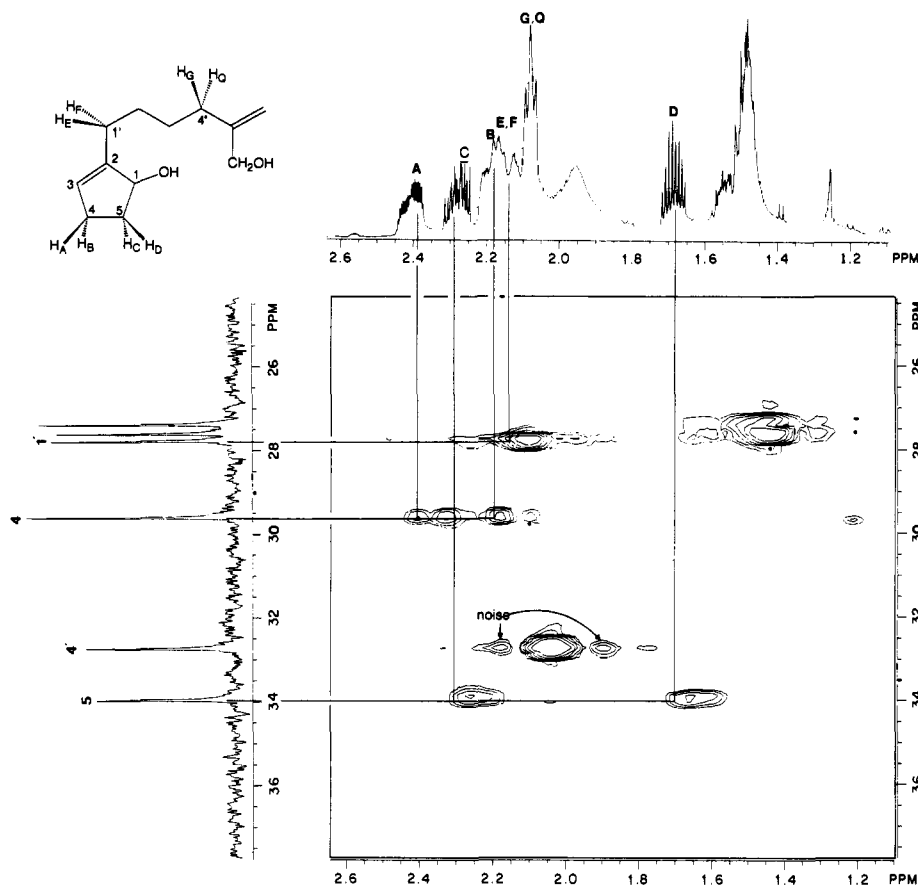


Figure 1. Two-dimensional proton-carbon shift correlated NMR spectrum.

Evidence to support the pickup of OH on the ring rather than on the exocyclic carbon, C1', was obtained by noting the characteristic five-membered carbonyl group stretch at 1740 cm^{-1} in the infrared spectrum of the ketone obtained from **2a** by protection of the primary allylic alcohol (*t*-BuPh₂SiCl, imidazole, CH₂Cl₂, room temperature), saturation of both π bonds (H₂, Pd/C), and oxidation (PCC/Celite, CH₂Cl₂).

The ¹³C NMR spectrum for **2a** displayed the expected 12 signals, including one at 65.77 and another at 78.80 corresponding to the methylene and methine hydroxyl-bearing carbons, respectively. Assignment of the ¹³C NMR signal appearing at 33.95 to C5 was possible using two-dimensional proton-carbon shift correlated spectroscopy, as portrayed in Figure 1. The diastereotopic protons attached to this carbon appear at distinctly different chemical shifts, 2.25 and 1.68, clearly indicating their different electronic environments.

Perhaps the most interesting assignment was the assignment of signals appearing at 2.38 and 2.15 in the ¹H NMR spectrum to the ring allylic carbon C4 rather than to the exocyclic position, C1'. This is made possible by using the ²H NMR spectrum of the diastereomeric diols **2b**, which are produced by subjecting **1b** to the conditions shown in eq 1. The spectrum displays signals at 2.33, 2.21, 2.13, and 1.61 for the deuterons. Those at 2.25 (2.25 for the corresponding proton) and 1.61 (1.68 for the corresponding proton) have already been assigned to the diastereotopic pair attached to C5. The other two signals were determined by proton-carbon correlation to be attached to a carbon resonating at 29.60. Since there is no doubt that the deuterons are appended to C4 and C5, the signal at 29.60 *must* correspond to C4, not C1'.

Variation of Solvent. Ether Formation. To test the generality of this process, we synthesized and examined the chemistry of diazene **3** which, while structurally similar to **1a**, does not contain

a dihydrophile capable of intercepting the intermediate intramolecularly.^{8a} We were never in doubt concerning the diazene's solubility in water at 75 °C or in water/*n*-propanol mixed solvent systems, for the polar OH and N=N units facilitate solubilization of this compound; even in water at room temperature, no sign of oil droplets was ever apparent.^{8b}

As illustrated in eq 2, heating an aqueous solution of **3** (1.5 mM) to 75 °C for 14 h afforded a 68% yield of a 5:1 mixture of diols **4a** and **5a**; the preferred product had the hydroxyl group appended to the five-membered ring rather than to the exocyclic carbon. Repetition of the experiment in D₂O led to the incorporation of one deuterium on the exocyclic carbon in **4a** and one at the allylic endocyclic carbon in **5a**, as expected. In contrast to the reactions conducted in an aqueous medium, the use of *n*-propanol as the solvent led to the nearly exclusive formation of dimers of the type commonly obtained from the combination of two triplet diradicals.⁹ Equation 4 indicates that the use of a mixed solvent system consisting of 30% *n*-PrOH/H₂O by volume leads to the formation of water-trapped product **4a** together with the analogous ether **4b**, the latter resulting from interception of the intermediate by *n*-PrOH. Notice that in both materials the OR (R = H and *n*-Pr) unit is bonded to the five-membered ring rather than to the first carbon exocyclic to it. Neither the re-

(8) (a) Compound **3** was synthesized in a manner analogous to that we have used previously. See, for example, refs 2 and 6. (b) Two other hydrocarbon diazenes were examined, specifically, compound **9** and another diazene with a (CH₂)₅ chain (i.e., a six-membered ring) in place of the geminal methyl groups at the exocyclic carbon; both undergo reaction with water. However, oil droplets could be seen when each was added to water at room temperature. While heating should facilitate solubilization, we were never completely certain that a homogeneous solution was obtained. Consequently, we do not consider the data obtained from these systems to be sufficiently reliable to use in formulating a mechanistic model.

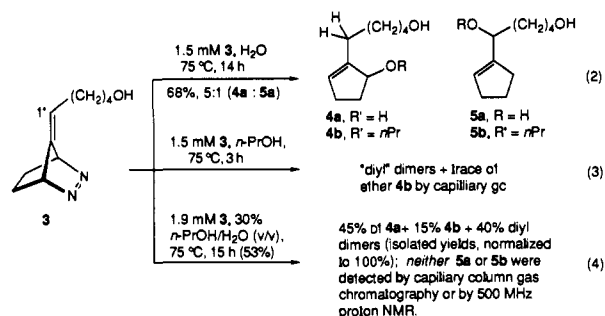
(9) (a) Similarly, only the previously defined products of intramolecular cycloaddition are obtained when diazene **1a** is heated in methanol,⁶ a solvent whose dielectric constant is close to that of *n*-PrOH. (b) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 4.

(7) If the hydroxyl group on the tether was closer to the reactive centers in the intermediate, then intramolecular trapping could provide additional evidence for the polar intermediate. This issue may be addressed experimentally in the future.

Table I. Summary of Results Obtained in Solvents of Differing Dielectric Constants¹⁰

solvent	dielectric constant at 60 °C ¹²	comments (time for disappearance of diazene)
water	67	intermediate is captured by water (14 h)
<i>n</i> -PrOH	16	not captured by <i>n</i> -PrOH (3 h)
30% <i>n</i> -PrOH/ water	48	captured by both solvents (14 h)

gioisomeric diol **5a** or the corresponding propyl ether **5b** could be detected.



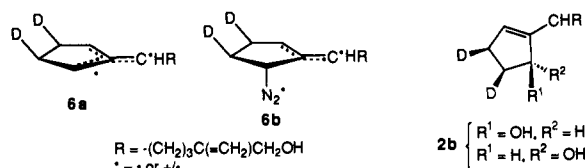
The latter results are consistent with a process involving proton abstraction from oxygen to generate "*n*-PrO⁻" and its subsequent capture at the positively polarized center or the alternative possibility where propanol attacks the intermediate first. *It is thermodynamically unlikely that any of the reactions leading to the capture of ROH originate from a diradical intermediate.* The formation of a new C-H bond is insufficient to compensate for both the loss of ca. 10 kcal/mol of resonance delocalization energy and the energy required to break an O-H bond homolytically.^{9b}

Role of Solvent Polarity.¹⁰ From the data summarized in Table I, we suggest that solvent polarity, expressed as the dielectric constant of the medium, plays a critical role in determining whether a purely diradical or a "dipolar diradical" pathway is followed.¹¹ It appears that when the dielectric constant of the medium is less than or equal to 16, diradical behavior is expressed; diyl dimerization or, for diazenes such as **1a** where a dylophile is present, intramolecular diyl trapping will occur. When it is greater than or equal to 48, dipolar reactivity prevails and the intermediate is intercepted in the heretofore unprecedented manner leading to the formation of alcohols and ethers. Except for the use of the nonnucleophilic solvent acetonitrile, we have not conducted experiments which allow commentary in the region of dielectric constants between 16 and 48. In acetonitrile, diyl dimerization occurs. Since the addition of water did not change the dielectric constant appreciably, studies were not conducted in acetonitrile/water.¹²

Examination of Table I also reveals that more time is required for diazene **3** to disappear when heated to 75 °C in solvents of high (>48 at 60 °C) rather than low dielectric constant, presumably due to ground-state stabilization of the diazene. One might have anticipated that the use of a more polar solvent would have led to stabilization of a polar intermediate and a rate acceleration, unless the ground state was stabilized more than the intermediate. *We believe that dipole-dipole and hydrogen bond interactions between the cis-disubstituted diazene and the solvent stabilize the ground state sufficiently to account for the retar-*

*dation.*¹³ As stated above, we consider it most unlikely that the pure zwitterionic state will ever lie below even the highest energy diradical without a very significant electronic perturbation.

A Nitrogen-Free Intermediate? To determine whether the intermediate was nitrogen-free as portrayed in **6a** or was simply one where a single C-N bond had undergone scission (**6b**), we synthesized and examined the chemistry derived from the C4-C5 deuterated diazene **1b**.¹⁴ If the intermediate has lost nitrogen and possesses a planar or time-average planar geometry, then attack of water should occur with equal probability from the top and bottom faces of the five-membered ring. If only a single C-N bond has been severed, then the faces will be different and there may be a preference for water to attack from the least hindered side, away from the CN₂^{*} unit. Analysis of the ²H NMR spectra of the product alcohols revealed the presence of four peaks, which integrated for the same number of deuteriums (i.e., 1:1:1:1), within experimental error. This result argues in favor of a nitrogen-free intermediate and the formation of equal amounts of diastereomers **2b**. The argument may be flawed in this case, however, because the CN₂^{*} unit may simply be too small to influence the approach of a small water molecule.



Another issue of interest is that the plane formed by HC*^{*}R shown above could be coplanar or orthogonal to the ring carbons. If the latter is so and the rotational barrier is high enough to preclude rotation under the conditions of the experiment, then one might anticipate preferential attack from the side away from the R group. However, R may be too far away from the site of attack by the small water molecule to serve as a steric bias. The present labeling studies, therefore, do not assist in determining the geometry at the exocyclic carbon.

Rationale. Role of a Bisected Dipolar Diradical. Why does the major product invariably correspond to the one where the OR unit is attached to the ring rather than to the exocyclic carbon? By what means is zwitterionic character assimilated into the intermediate?

In principle, the zwitterionic resonance form of the singlet diyl could assume either a planar or a bisected geometry. The bisected and planar forms of the parent diradical, trimethylenemethane (TMM), are calculated to differ in energy by as little as 2.4^{4c} and as much as 6.9 kcal/mol;¹⁵ in each case, the bisected form is of lower energy. Calculations also indicate that the bisected singlet lies below the coplanar form of the isopropylidene diyl derived from diazene **9** shown in eq 5.⁴ We assumed that the bisected singlet was also of lower energy for the systems referred to herein and have therefore focused upon the formulation of two possible zwitterionic forms possessing this geometry. However, calculations place the coplanar zwitterionic state below that of the orthogonal form for the parent TMM.¹⁶ We argue that the presence of the alkyl chain on the carbon exocyclic to the five-membered ring in **7** leads to an energy-raising allylic 1,3-interaction and a reversal of the ordering for its zwitterionic state. A similar argument involving a steric destabilization of the planar form of the dimethyl-substituted diyl **8** has been offered by Davidson and Borden.¹⁶

(13) (a) A recent discussion of the effect of hydroxylic solvents on the rate of disappearance of acyclic *cis*-diazene has appeared: Neuman, R. C., Jr.; Berge, C. T.; Binegar, G. A.; Adam, W.; Nishizawa, Y. *J. Org. Chem.* **1990**, *55*, 4564. See also: (b) Mirbach, M. J.; Liu, K.-C.; Mirbach, M. F.; Cherry, W. R.; Turro, N. J.; Engel, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 5122. Schulz, A.; Rüchardt, C. *Tetrahedron Lett.* **1976**, 3883. (c) Engel, P. *Chem. Rev.* **1980**, *80*, 99. (d) Jung, M. E.; Gervay, J. *J. Am. Chem. Soc.* **1989**, *111*, 5469.

(14) (a) Little, R. D.; Billera, C. F. *Tetrahedron Lett.* **1988**, *29*, 5711. (b) Stone, K. J.; Little, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2495.

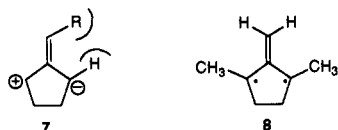
(15) *Electrons in Chemical Reactions - First Principles*; Salem, L., Ed.; Wiley: New York, 1982; p 92.

(16) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1977**, *99*, 2053.

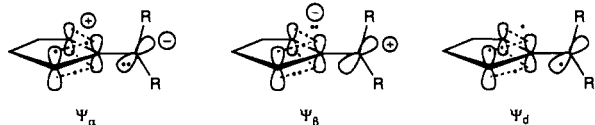
(10) The present discussion could have been formulated using several solvent polarity scales including, for example, the E_T scale of Reichardt and Dimroth and the related RPM scale of Dähme and co-workers. We selected dielectric constant because of the wealth of existing data for binary solvent systems as a function of temperature.¹² (a) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 98. (b) Dähme, S.; Shob, F.; Nolte, K.-D.; Radeaglia, R. *Ukr. Khim. Zh. (Russ. Ed.)* **1975**, *41*, 1170; *Chem. Abstr.* **1976**, *84*, 43086j.

(11) The idea of radicals possessing polar character is well known. For an interesting discussion and a host of references, see: Wentrup, C. *Reactive Molecules, The Neutral Reactive Intermediates in Organic Chemistry*; Wiley-Interscience: New York, 1984; particularly section 2.5.5.

(12) Akhadov, Y. Y. *Dielectric Properties of Binary Solutions*; Pergamon: Oxford, 1981.

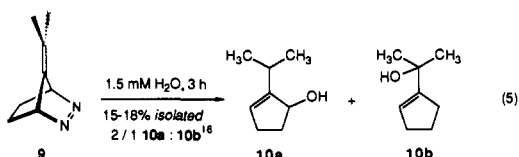


Of the zwitterionic formulations, a bisected form consisting of a two-electron allyl cation on the ring and an orthogonally-oriented carbanion at the exocyclic carbon (Ψ_α) should be of lower energy than the alternative formulation consisting of a four-electron allyl anion and a positive charge on the orthogonal exocyclic carbon (Ψ_β).¹⁷ To the extent that this resonance form (valence bond



structure) contributes to the overall character of the intermediate, zwitterionic character is built into its wave function and the reactivity pattern of the intermediate.^{1b} Ψ_α and Ψ_β represent the zwitterionic formulations illustrated above, while α and β indicate how much of the character of each is mixed into the total wave function, Ψ , which is represented by $\alpha\Psi_\alpha + \beta\Psi_\beta + \delta\Psi_\delta$, where $\delta\Psi_\delta$ is included to acknowledge the fact that the wave function cannot, according to the discussion given above, be strictly ionic. The Ψ_δ term, therefore, represents the diradical contribution to the overall wave function. Clearly, the contribution of the zwitterionic form should increase in response to the polarity demands imposed by the solvent, and we think this is the case. The suggestion of an orthogonal intermediate also allows one to understand why ROH-trapped products with a double bond exocyclic to the ring have not been detected.

If one assumes that this assessment is accurate, then it is easy to understand why the negatively polarized OR unit attaches predominantly to the positively polarized ring rather than the exocyclic carbon. Yet, as shown in eq 2 and evidenced by the formation of alcohol **5a**, "OH" also attacks the exocyclic carbon. This, we believe, argues for a small contribution to Ψ of resonance formulation Ψ_β . The relative contributions of Ψ_α and Ψ_β , given by the sizes of α and β , should vary as a function of R, the substituent attached to the exocyclic carbon. In particular, the presence there of two rather than one alkyl group should increase β relative to α and lead to an increase in the amount of product with an OH attached to the exocyclic carbon. The result shown in eq 5 for the dimethyl diazene **9** is consistent with this view.^{7b,18}



Here, the ratio of ring to exo OH pickup is 2:1, rather than the 5:1 ratio which is expressed by the monoalkyl substituted system **3** illustrated in eq 2. While the mass balance is low due to the volatility of the products **10a** and **10b**, we are confident that their ratios are accurate. As outlined in the Experimental Section, the structure of **10b** was confirmed by independent synthesis.

Experimental Section

General Procedures. A description of the methods used for solvent purification, performing chromatography, and the recording of data has been provided by us previously; see, for example, ref 6.

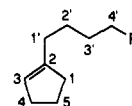
The ¹H-¹³C shift correlated spectroscopy experiment was performed using a pulse sequence: ¹H, 90°_{φ1}-t₁-Δ₁-90°_{φ2}-τ-Δ₂-decouple, ¹³C, t₁/2-180°_{φ1}-t₁/2-Δ₁-τ-90°_{φ3}-τ-Δ₂-acquisition_{φR}, with a 90° (¹³C) pulse of 13.5 ms and a 90° (¹H) pulse of 30 μs calibrated before the experiment. To afford quadrature detection in both frequency domains,

(17) For a general discussion of "resonance interactions in acyclic systems" as well as a set of references dealing with both experimental and theoretical aspects of allyl cations and anions, see: Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61.

(18) The low yield of **10a** and **10b** is a reflection of their volatility. The structures of these compounds were confirmed by independent synthesis.

an eight-step phase cycling has been applied.¹⁹ Spectral data were collected into 2K data blocks for 256 t₁ increments with a relaxation delay of 2.0 s, Δ₁ = 3.7 ms, Δ₂ = 2.1 ms, τ = 10 μs. Spectral width was 20833.3 Hz in the first dimension and 4132.2 Hz in the second dimension. The data matrix was zero filled to 1K and apodized with an exponential function to give a line broadening of 2 Hz in both directions.

The carbon numbers which appear in the ¹³C NMR data refer to the numbering system shown below.



Diazenes 1a and 1b. Details for the preparation of **1a**, as well as spectral data which characterize it, can be found in ref 6. Deuterated diazene **1b** was prepared in a manner entirely analogous to that used for **1a**, except that AcOD was substituted in place of AcOH in the generation of diimide.

Diazene 3. The bis(dimethyl azodicarboxylate) precursor (665.8 mg, 2.23 mmol), prepared in accord with methods described by us previously,⁶ was dissolved in ethanol (20 mL, 0.11 M). Potassium hydroxide (2.25 g, 40.14 mmol) was added, and the solution was heated at reflux for 45 min. The solution was then cooled to 0 °C, and an aqueous solution of K₃Fe(CN)₆ (0.3 M), also at 0 °C, was added dropwise. This was allowed to stir at 0 °C for 20 min, the aqueous layer was extracted with Et₂O (5 × 15 mL), the Et₂O layer was dried, and the solvent was removed in vacuo. The residual oil was chromatographed on silica gel with 50, 55, 60, 65, 70, 75, and 80% Et₂O/petroleum ether (v/v) to give 214 mg (54%) of pure diazene: IR (neat) 3680-3100 (br s OH), 2940, 2860, 1770-1690 (br and low intensity), 1065 (m) 1040 cm⁻¹; ¹H NMR (500 MHz) δ 5.39 (d, J = 1.88, 1 H, vinyl), 5.11 (t, J = 9.00, 2 H, bridge-heads), 3.61 (t, J = 6.50, 2 H, CH₂OH), 2.01 (m, 2 H, allylic), 1.78 (br s, 1 H, OH), 1.65 (m, 2 H), 1.49 (m, 2 H), 1.42 (m, 2 H), 1.12 (d, J = 10, 2 H, exo ring), 1.10 (d, J = 10, 2 H, endo ring); ¹³C NMR (125 MHz) δ 144.86 (C7), 117.17 (C5'), 72.53, 62.38, 31.90, 29.62, 28.67, 25.56, 21.44, 21.00; LRMS (EI) m/z 152 (M - 28), 150, 134, 117, 105, 93, 91 (base), 79, 71, 67, 53; exact mass [HRMS (CI)] calcd for C₁₀-H₁₆O (M - N₂) 152.1202, found 152.1196.

General Procedure for the Aqueous Trapping Reactions. The diazene was transferred in ether to a tared round-bottomed flask which was fitted with a reflux condenser and an inert gas inlet. The ether was removed in vacuo, and the flask was reweighed. Water was added to adjust the concentration of the diazene to the values listed in the equations, frequently 1.5 mM. After being degassed with argon for 0.5 h, the flask was immersed in a preheated (85 °C) oil bath; after equilibration, the temperature in the aqueous medium was determined to be 75 °C. The solutions were heated for the times listed in the equations and cooled to room temperature, and solid NaCl (~10 g) was added. The aqueous layer was extracted (Et₂O, 5 × 35 mL), and the ethereal layer was dried (MgSO₄) and concentrated in vacuo. The resulting material was then chromatographed on silica gel.

Diol 2a: TLC (20% CH₂Cl₂/petroleum ether) R_f 0.12, *p*-anisaldehyde (stains dark blue); IR (neat) 3500-3200, 2940, 2860, 1655, 1450, 1320, 1080, 945, 890, 860 cm⁻¹; ¹H NMR (500 MHz) δ 5.53 (s, 1 H, C2 vinyl), 5.02 (s, 1 H, vinyl), 4.87 (s, 1 H, vinyl), 4.63 (m, 1 H, CHOH), 4.07 (s, 2 H, CH₂OH), 2.38 (6' allylic), 2.25 (m, 1 H, C3 allylic), 2.15 (m, 2 H), 2.13 (m, 1 H), 2.06 (t, J = 7.0, 2 H, C3' allylic), 1.90 (s, 1 H, OH), 1.68 (m, 1 H), 1.55 (m, 2 H), 1.49 (m, 2 H), 1.30 (s, 1 H, OH); ¹³C NMR (125 MHz) δ 149.02 (C5'), 146.16 (C2), 127.06 (C3), 109.18 (CH₂, olefinic), 78.80 (CHOH), 65.77 (CH₂OH), 33.95 (C5), 32.73 (C4'), 29.60 (C4), 27.77 (C1'), 27.59, 27.37; LRMS (EI) m/z 178 (M - 18), 147, 131, 123, 117, 105, 97, 93, 83 (base), 79, 67, 55, 43; exact mass [HRMS (EI)] calcd for C₁₂H₁₈O (M - 18) 178.1358, found 178.1339. Anal. Calcd for C₁₂H₂₀O₂: C, 73.42; H, 10.27. Found: C, 71.71; H, 10.12.

Diastereomeric Diols 2b from the Reaction of 1b with Water. The compound was purified on silica gel using 60% Et₂O/petroleum ether as the eluting solvent: TLC R_f = 0.12, 30% Et₂O/CH₂Cl₂, *p*-anisaldehyde (stains dark blue); IR (neat) 3600-3100 (broad, OH), 2920, 2845, 2160 (C-D), 1640, 1455, 1445, 1425, 1300, 1075, 1025, 890, 725 cm⁻¹; ¹H NMR (500 MHz) δ 5.50 (m, 1 H, C₃ vinyl), 5.00 (s, 1 H, vinyl), 4.84 (s, 1 H, vinyl), 4.61 (d, J = 6 Hz, 1 H, CHOH), 4.03 (s, 2 H, CH₂OH), 2.56 (broad s, 1 H, allylic), 2.34 (s, 1 H), 2.17-2.05 (m, 6 H), 1.60 (m, 1 H), 1.55-1.40 (m, 5 H); ²H NMR (76.77 MHz) proton decoupled δ 2.33 (s, 1 D, allylic), 2.20 (s, 1 D, homoallylic), 2.13 (s, 1 D, homoallylic), 1.61 (s, 1 D, allylic), the region between ca. 1.2 and 2.8 ppm is illustrated

(19) Martin, G. E.; Zektzer, A. S. *Two-Dimensional NMR Methods for Establishing Molecular Connectivity*; VCH Publishers: New York, 1988.

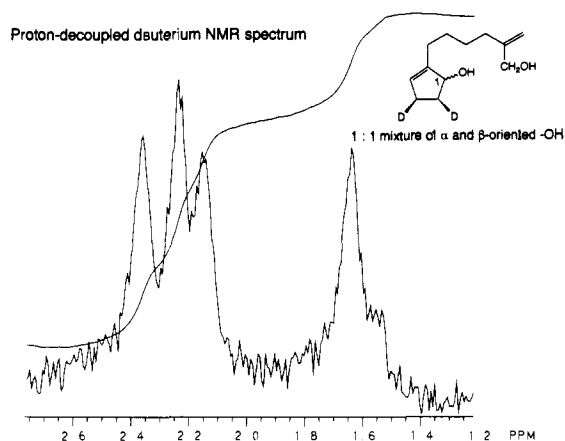


Figure 2. Proton-decoupled deuterium NMR spectrum.

in Figure 2; ^{13}C (125 MHz) δ 148.93 (C_5), 146.15 (C_2), 126.74 (C_3), 108.94 (exocyclic $\text{CH}_2=\text{C}$), 78.47 (CHOH), 65.44 (CH_2OH), 33.65 (C_5), 32.62 (C_4'), 29.60 (C_4), 27.77 (C_1'), 27.51, 27.26; LRMS (EI) m/z 180 ($\text{M} - 18$), 179 (base), 178, 161, 148, 132, 120, 106; exact mass [HRMS (EI)] calcd for $\text{C}_{12}\text{H}_{16}\text{OD}_2$ ($\text{M} - 18$) 180.1522, found 180.1482.

Diol 4a: TLC (80% EtOAc/ CHCl_3) R_f = 0.18 *p*-anisaldehyde (stains dark blue); IR (neat) 3630–3120 (broad OH), 2940, 2860, 1570, 1370, 1050 cm^{-1} ; ^1H NMR (500 MHz) δ 5.53 (broad s, 1 H, vinyl), 4.64 (broad s, 1 H, CHOH), 3.64 (t, J = 6.5, 2 H, CH_2OH), 2.41 (m, 1 H, allylic), 2.30 (m, 1 H, allylic), 2.18 (m, 4 H), 1.72 (m, 4 H), 1.59 (m, 2 H), 1.40 (apparent quartet, J = 7.8, 2 H); ^{13}C NMR (125 MHz) δ 146.15 (C_2), 127.10 (C_3), 78.53 (CHOH), 62.54 (CH_2OH), 33.72, 32.24, 29.32, 27.68, 27.14, 25.35 (C_3'); LRMS (EI) m/z 152 ($\text{M} - \text{H}_2\text{O}$), 134, 119, 106, 97, 93, 83, 80 (base), 77, 67, 55; exact mass [HRMS (EI)] calcd for $\text{C}_{10}\text{H}_{16}\text{O}$ ($\text{M} - \text{H}_2\text{O}$) 152.1201, found 152.1204.

Reaction of 3 in 30% *n*-PrOH/Water. Formation of 4a and 4b. To the diazene (122 mg, 0.677 mmol) was added 30% *n*-propanol in water (v/v, 350 mL, 1.9 mM). The solution was degassed with argon for 30 min and then heated at 75 °C for 15 h. NaCl (~10 g) was added, and the reaction mixture was extracted with Et_2O (5×40 mL). The organic layer was dried, the extracting solvent was removed in vacuo, and *n*-propanol was removed via vacuum distillation at room temperature. Chromatography on silica gel with 10 and 15% ethyl acetate in methylene chloride (v/v) afforded 11.2 mg (8%) of the propyl ether 4b [TLC: R_f = 0.44 (100% Et_2O), *p*-anisaldehyde], 27.5 mg (24%) of diol 4a, and 42.8 mg (21%) of diyl dimers. The spectral data for compound 4a is reported above.

4b: FTIR (CHCl_3) 3628 (sharp, OH), 3080, 3060, 3045, 2940, 2860, 1465, 1340, 1260, 1170, 1080, 1056, 790 cm^{-1} ; ^1H NMR (500 MHz) δ 5.54 (m, 1 H, vinyl), 4.34 (m, 1 H, CHOH), 3.67 (t, J = 6.6, 2 H, CH_2OH), 3.44 (dt, J = 9.1, 6.5, 1 H, CHOCH_2), 3.30 (dt, J = 9.0, 6.8, 1 H, CHOCH_2), 2.37 (m, 1 H, allylic), 2.16 (m, 6 H), 1.78 (m, 1 H), 1.64 (m, 6 H), 1.26 (s, 1 H, OH), 0.96 (t, J = 6.56, 3 H, CH_3); ^{13}C NMR (75 MHz) δ 127.78 (C_3), 86.24 (C_1), 70.69 (ROCH_2), 63.43 (C_5'), 33.08, 30.50, 30.32, 28.76, 27.79, 26.11, 23.77, 11.19 (CH_3); LRMS (EI) m/z 212 (M), 152 ($\text{M} - \text{C}_3\text{H}_7\text{O}$), 139, 134, 125, 119, 105, 97, 93, 83 (base), 79, 71, 67, 59, 55; exact mass [HRMS (EI)] calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2$ (M) 212.1776, found 212.1796.

Reaction of 3 in D_2O . To diazene 3 (65.5 mg, 0.363 mmol) was added deuterium oxide (182 mL, 2.0 mM). The solution was degassed with argon for 30 min and then heated at 75 °C for 15 h. NaCl was added, and the mixture was extracted with Et_2O (7×40 mL). The ethereal layer was dried and concentrated in vacuo; the residue was chromatographed on silica gel with 70, 75, and 80% Et_2O /petroleum ether to afford a 53% yield (33.1 mg, 0.193 mmol) of deuterated product.

4a- d_1 (deuterium attached to C_1'): IR (neat) 3650–3100 (broad, OH), 2950, 2870, 2140 (C–D), 1650, 1460, 1438, 1320, 1310, 1050, 930, 840 cm^{-1} ; ^1H NMR (500 MHz) δ 5.49 (m, 1 H, vinyl), 4.60 (m, 1 H, CHOH), 3.60 (t, J = 6.5, 2 H, CH_2OH), 2.36 (m, 1 H, allylic), 2.26 (m, 1 H), 2.18–1.84 (5 H), 1.56 (m, 2 H), 1.42 (m, 2 H), 1.36 (m, 2 H); ^2H NMR (76.77 MHz) δ 2.09; ^{13}C NMR (125 MHz) δ 146.11 (C_2), 127.05 (C_3), 78.73 (C_1), 62.76 (C_5'), 33.96, 32.47, 29.57, 27.34, 27.30, 25.58; LRMS (EI) m/z 171 (M), 153 ($\text{M} - \text{H}_2\text{O}$), 135, 124, 119, 106, 90, 83 (base), 80, 71, 67, 55, 43; exact mass [HRMS (EI)] calcd for $\text{C}_{10}\text{H}_{17}\text{DO}_2$ 171.1370, found 171.1350.

The evidence in support of the formation of the minor product 5a- d_1 (deuterium attached to ring) is less compelling. Integration of the olefinic peaks for this and the major isomer 4a- d_1 indicates that they are formed in a ratio of 4:1 (5:1 by capillary column GC). 5a- d_1 : ^1H NMR (500 MHz) δ 5.39 (m, 1 H, vinyl), 5.11 (m, 1 H, CHOH), 3.60 (t, J = 6.5, 2 H, CH_2OH), 1.47 (t, J = 7.4, 2 H). There is only one peak in its deuterium NMR spectrum. Additional support for the assignment comes from a comparison of the data with its undeuterated counterpart 5a, whose mass spectral fragmentation pattern is nearly identical to that of 4a. 5a: LRMS (EI) m/z 152 ($\text{M} - \text{H}_2\text{O}$), 134, 119, 105, 93, 91, 80 (base), 79, 77, 67, 55, 53, 51, 44.

Reaction of 3 in *n*-PrOH. Diazene 3 (55.6 mg, 0.308 mmol) was dissolved in *n*-propanol (205 mL, 1.5 mM); the solution was degassed (Ar, 30 min) and heated at 75 °C for 3 h. *n*-Propanol was removed in vacuo, and the residue was analyzed by gas chromatography and ^1H NMR spectroscopy. The main products were diyl dimers (44.7 mg, 50%), but a trace (<1%) of ether 4b was also observed by capillary GC.

Alcohol 10a: TLC (30% Et_2O /petroleum ether) R_f = 0.28, *p*-anisaldehyde (stains dark blue); IR (CDCl_3) 3144, 2990, 2965, 2910, 1840, 1790, 1720 (very weak), 1560, 1470, 1385, 1250, 1170, 1100 cm^{-1} ; ^1H NMR (500 MHz) δ 5.90 (m, 1 H, vinyl), 5.71 (m, 1 H, CHOH), 2.78 (m, 1 H, allylic), 2.34 (m, 2 H, allylic, $(\text{CH}_3)_2\text{CH}$), 1.93 (m, 1 H, homoallylic), 1.72 (m, 1 H, homoallylic), 1.46 (s, OH), 1.19 (d, J = 14.5, 6 H, CH_3); ^{13}C NMR (125 MHz) δ 133.65 (C_3), 130.83 (C_2), 57.34 (CHOH), 32.56 ($\text{CH}(\text{CH}_3)_2$), 28.01, 27.06 (CH_3), 24.70; LRMS (EI) m/z 126 (M), 111 ($\text{M} - \text{CH}_3$), 109, 67, 59 (base); exact mass [HRMS (EI)] calcd for $\text{C}_8\text{H}_{14}\text{O}$ (M) 126.10452, found 126.1066.

Alcohol 10b: TLC (30% Et_2O /petroleum ether) R_f = 0.28, *p*-anisaldehyde (stains dark blue); IR (CDCl_3) 3618, 2965, 2940, 2840, 1840, 1820, 1650, 1470, 1385, 1370, 1325, 1255, 1200, 1165, 1105 cm^{-1} ; ^1H NMR (500 MHz, CCl_4) δ 5.34 (m, 1 H, vinyl), 2.36 (m, 4 H, allylic), 2.15 (s, 1 H, OH), 1.90 (m, 2 H, homoallylic), 1.34 (s, 6 H, $(\text{CH}_3)_2\text{COH}$); ^{13}C NMR (125 MHz, CCl_4) δ 151.52 quaternary olefinic carbon, 122.40 (vinyl carbon) 70.57 ($\text{C}(\text{CH}_3)_2\text{OH}$), 32.37 (C_1), 31.60 (C_4), 29.09 (CH_3), 23.73 (C_5); LRMS (EI) m/z 126, 111 (base) ($\text{M} - \text{CH}_3$), 108 ($\text{M} - \text{H}_2\text{O}$), 93, 91, 83, 79, 77, 71, 67, 65, 59, 57, 55, 45; exact mass [HRMS (EI)] calcd for $\text{C}_8\text{H}_{14}\text{O}$ (M) 126.1045, found 126.1031.

Confirmation of Structure 10b by Independent Synthesis. A solution of 1-(tri-*n*-butylstannyl)cyclopentene (832 mg, 2.33 mmol) in Et_2O (6.2 mL, 0.37 M) was cooled to –65 °C.²⁰ *n*-Butyllithium (1.11 mL of 2.1 M in hexane, 2.33 mmol) was added. This was stirred for 1 h at –65 °C and for 2 h at room temperature. The reaction mixture was cooled to 0 °C, and acetone (0.35 mL, 16.1 mmol), which had been freshly distilled from B_2O_3 , was added. The reaction mixture was allowed to warm to room temperature. Cold saturated NH_4Cl was added, and the product was extracted with Et_2O (5×25 mL). The organic layer was dried with aqueous NaCl and Na_2SO_4 , and the solvent was removed by distillation. The compound was isolated by chromatography using 20% Et_2O /petroleum ether as the eluting solvent. The solvent was carefully removed via distillation. When most of the solvent was removed, CCl_4 (5 mL) was added, and the distillation was continued until all but the CCl_4 and some of the alcohol remained. The spectral data matched those reported above.

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Registry No. 1a, 125877-59-0; 1b, 139244-21-6; 2a, 139244-16-9; 2b (isomer 10), 139244-20-5; 2b (isomer 2), 139344-78-8; 3, 139244-17-0; 4a, 139244-18-1; 4a- d_1 , 139244-23-8; 4b, 139244-22-7; 5a, 139244-19-2; 9, 31689-32-4; 10a, 139276-04-3; 10b, 90112-28-0; H_2O , 7732-18-5; *n*-PrOH, 71-23-8; 1-(tributylstannyl)cyclopentene, 91897-90-4; acetone, 67-64-1.

Supplementary Material Available: Proton NMR data for compounds 4a, 5a, 4a- d_1 , and 5a- d_1 , along with mass spectra for compounds 4a and 5a (6 pages). Ordering information is given on any current masthead page.