

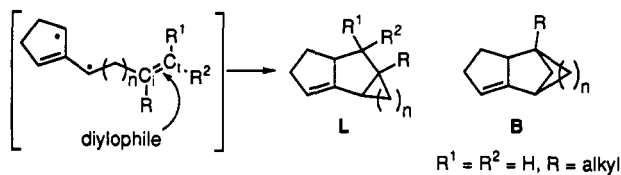
## Intramolecular Diyl Trapping Chemistry: Diyl-Decoupling and 7-endo-trig Cyclization

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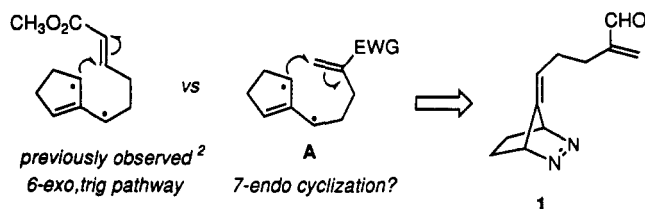
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We recently reported the results of a study designed to determine how the intramolecular diyl trapping reaction is influenced by the location and electronic properties of substituents appended to the diylophile.<sup>1</sup> The presence of an electron-withdrawing group (EWG) at either the internal (C<sub>i</sub>) or terminal (C<sub>t</sub>) carbon leads to linearly fused cycloadducts (L) arising *via* the singlet manifold. On the other hand, the presence of an alkyl group on the internal carbon shifts the chemistry from the singlet to the triplet diyl, the latter leading predominantly to the formation of bridged cycloadducts (B). The larger the alkyl group, the more substantial the triplet contribution and the greater the yield of bridged materials.

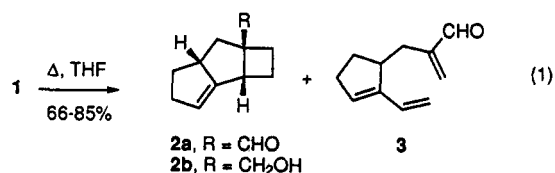


These generalizations refer to cases wherein the length of the tether linking the diyl to the diylophile is three carbons long, *i.e.*, when  $n = 3$ . When  $n = 2$ , experience has shown us that triplet chemistry dominates even when the terminal carbon bears an electron-withdrawing group.<sup>2</sup> We wondered whether the same would be true when an electron-withdrawing group was appended to the internal carbon and if so, what mode of initial cyclization would predominate, the 6-*exo* mode previously observed or a 7-*endo* pathway, it being facilitated by the radical-stabilizing characteristics of the electron-withdrawing group. To examine these issues, we synthesized diyl precursor 1 in a manner entirely analogous to that which



we have used previously.<sup>1-3</sup> We report the results of our efforts at this time.

Heating diazene 1 for 3 h at 67 °C in THF leads cleanly to the formation of the *cis,syn*-tricyclic 2a and triene 3 in the ratio 1.6–1.65:1. Analysis by GC, TLC, and <sup>1</sup>H NMR



spectroscopy indicates that these were the only materials formed. It is noteworthy that only the *cis,syn* tricyclic isomer was isolated; the *cis,anti* linearly fused isomer generally dominates in diyl trapping reactions.<sup>1,3</sup> This case is the first example of an intramolecular diyl trapping reaction where only one stereoisomer is formed.

The most compelling evidence in support of the assignment comes from the NOE experiments which are summarized below for alcohol 2b. Notice, in particular, the substantial effect on H<sub>r</sub> and H<sub>x</sub> which is observed upon irradiation of H<sub>i</sub> ("H<sub>i</sub>" refers to the methylene protons of the hydroxymethylene unit).

irradiate →	H <sub>i</sub>	H <sub>r</sub>	H <sub>x</sub>
	observe ↓		
H <sub>i</sub>	---	0	1.3
H <sub>r</sub>	9.4	---	8.3
H <sub>x</sub>	16.8	2.5	---

Oxygen quenching studies were conducted to determine whether adducts 2a and 3 are derived from the singlet and/or the triplet diyl.<sup>1,12</sup> A control experiment demonstrated the products to be stable under the reaction conditions. Thus, when a steady stream of oxygen was bubbled through a 10<sup>-3</sup> M solution of 1 heated to 67 °C in THF, *no triene* 3 was isolated. This suggests that 3 is derived exclusively from the triplet manifold. Furthermore, the yield of tricyclic 2a drops from 62% in the absence of O<sub>2</sub> to 34% in its presence. Assuming complete quenching of the triplet, and that the lifetime of the singlet is too short to be intercepted by oxygen,<sup>1a,4</sup> then the amount of 2a produced in the presence of oxygen indicates the amount of 2a which is singlet derived. The amount arising from the triplet is given by the difference between how much is formed in oxygen's absence (*i.e.*, the amount coming from both S and T) and the amount derived exclusively from the singlet, *viz.*, 62–34 = 28%. The triplet, therefore, affords 28% of 2a and 38% of triene 3, the latter value corresponding to the quantity of triene produced in the absence of the quenching agent. We conclude that the initially formed trimethylenemethane (TMM) singlet diyl partitions between intersystem crossing (ISC; 66%) and cyclization to afford 2a (34%), while 42% of the triplet closes to 2a and 58% opens to afford 3.

We suggest the explanation illustrated in Scheme 1 to account for the results. The observed *cis,syn* selectivity presumably derives from the fact that the TMM diyl initially generated from 1 is likely to be the bisected singlet

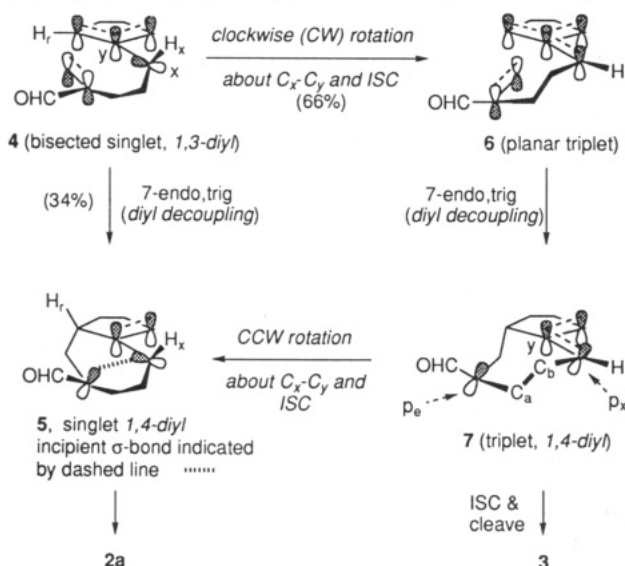
(1) (a) Masjedizadeh, M. R.; Dannecker-Doerig, I.; Little, R. D. *J. Org. Chem.* 1990, 55, 2742. (b) Little, R. D.; Masjedizadeh, M. R.; Moeller, K. D.; Dannecker-Doerig, I. *Synlett* 1992, 107.

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## Scheme 1. Partitioning of the Initially Formed Diyl 4



4.5 This geometry predisposes the tether and diylophile so that upon 7-endo-trig cyclization to afford 5, hydrogens  $H_x$  and  $H_r$  are oriented cis to one another.<sup>6</sup> In addition, the p-orbital located on the carbon exocyclic to the five-membered ring, and the odd electron center positioned  $\alpha$  to the aldehyde, are pointed toward one another in a manner which ought to facilitate formation of the *cis,syn* adduct 2a. Competitive intersystem crossing (ISC) from the bisected singlet 1,3-diyl 4 to the planar triplet 6, followed by 7-endo-trig cyclization, leads to the triplet 1,4-diyl 7.<sup>7</sup> Here, the p-orbitals  $p_x$  and  $p_e$  are parallel to the intervening sigma bond,  $C_a-C_b$ , and are therefore stereoelectronically well-suited to facilitate cleavage of that bond leading to the formation of triene 3.<sup>7,8</sup> Notice that the geometric change from the bisected to the planar TMM (4 to 6), and between the 1,4-diyls 7 and 5, involves rotation about the bond,  $C_x-C_y$ . It is reasonable that these rotations should promote the spin-orbit coupling needed to facilitate intersystem crossing.<sup>9</sup>

(5) For a discussion of the geometry associated with the singlet and triplet forms, refer to: (a) Berson, J. A. In *Diradicals*; Borden, W. T.; Wiley: New York, 1982; Chapter 4. (b) Little, R. D.; Brown, L. M.; Masjedizadeh, M. R. *J. Am. Chem. Soc.* 1992, 114, 3071. (c) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* 1977, 99, 2053.

(6) While it is convenient to describe TMM diyl olefin additions by using the Baldwin descriptors, the reactions of the endocyclic radical of the TMM diyl have little in common with reactions of linear alkenyl radicals upon which those rules were based. First, the diradical portions of both singlet and triplet diyls possess fixed geometries. Any conformational equilibration required for intramolecular reactions of TMM diyls is therefore limited to movements of atoms in the tether. In contrast, linear alkenyl radicals may freely rotate about any bond. In addition to the decreased conformational range of the TMM diyls, the inherent  $sp^2$  hybridizations of both the singlet and triplet diradicals make comparisons to other systems difficult. The preferences of monoradical reactions are quite sensitive to such differences in hybridization. See, for example: Curran, D. P.; Chang, C.-T. *J. Org. Chem.* 1989, 54, 3140 and references cited therein. This paper also provides examples of 7-endo ring closure in monoradical cyclization. See also: Balchi, M. D.; Frolow, F.; Hoornaert, C. *J. Org. Chem.* 1983, 48, 1841. Batty, D.; Crich, D. *Tetrahedron Lett.* 1992, 33, 875. Snider, B. B.; Merritt, J. E. *Tetrahedron* 1991, 47, 8663.

(7) (a) Characteristic reactions of 1,4-diyls are described: Dervan, P. B.; Dougherty, D. A. In *Diradicals*; Borden, W. T.; Wiley: New York, 1982; Chapter 3. See also: (b) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* 1972, 94, 7500. (c) Wagner, P. J. *Acc. Chem. Res.* 1971, 4, 168. (d) Engel, P. S.; Horsey, D. W.; Keys, D. E.; Nalepa, C. J.; Soltero, L. R. *J. Am. Chem. Soc.* 1983, 105, 7108. (f) McElwee-White, L.; Dougherty, D. D. *J. Am. Chem. Soc.* 1984, 106, 3466. (g) Samuel, C. J. *J. Chem. Soc., Perkin Trans. 1* 1989, 1259. *Lifetimes of 1,n-diyls and factors influencing them*, see ref 5a above and: Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* 1989, 89, 521.

(8) For a recent discussion of stereoelectronic effects, see: Berson, J. A. *Acc. Chem. Res.* 1991, 24, 215 and references cited therein.

In summary, we have observed the first 7-endo-trig cyclization of a trimethylenemethane diradical. The presence of the electron-withdrawing group on the internal carbon of the diylophile in 1 is apparently sufficient to enforce a stepwise process which serves to decouple the TMM odd-electron centers, despite the attendant loss in TMM delocalization energy (note Scheme 1). The resulting 1,4-diyl partitions between  $\sigma$  bond formation to afford selectively the *cis,syn* tricycle 2a, and cleavage of the intervening  $\sigma$ -bond,  $C_a-C_b$ , leading to triene 3. We intend to explore the generality of the decoupling process as a means to gain access to a variety of 1,n diradicals.

## Experimental Section

Proton NMR data were recorded at 500 MHz and are referenced to  $Me_4Si$ , while carbon-13 data were obtained at 125 MHz and are referenced to the center line of the  $CDCl_3$  pattern.  $J$  values are given in Hz. Standard procedures for solvent purification, chromatography, fulvene formation, and subsequent conversion to diazenes such as 1 have been described in previous publications.<sup>1-3,10</sup>

**Dimethyl 2,3-Diaza-7-[4'-[[4-methoxybenzyl]oxy]methyl]pent-4'-enylidene]bicyclo[2.2.1]heptane-2,3-dicarboxylate.** 6-[3'-[[4-(Methoxybenzyl)oxy]methyl]-3'-butenyl]fulvene (5.01 g, 17.8 mmol), prepared using a fulvene-forming methodology developed in these laboratories,<sup>10</sup> was dissolved in  $CH_2Cl_2$  (75 mL), and the resulting solution was cooled using an ice-water bath. Diethyl azodicarboxylate (3.07 mL, 19.5 mmol) was added dropwise. The reaction was placed in a refrigerator ( $\approx 5^\circ C$ ) until monitoring by TLC or  $^1H$  NMR indicated completion. The crude Diels-Alder adduct was then reduced directly. Additional  $CH_2Cl_2$  (100 mL) was added to the reaction vessel. Dipotassium azodicarboxylate (22.0 g, 0.113 mol) was added, and the mixture was vigorously stirred and cooled using an ice-water bath. Acetic acid (16.3 mL, 0.281 mol) was carefully added dropwise over 0.5 h. The solution was stirred for 1.0 h (ice-water bath) after the addition of the acid was complete. The mixture was filtered, and the filter cake was washed well with  $CH_2Cl_2$ . The combined filtrates were concentrated *in vacuo* and chromatographed (25% to 50%  $Et_2O$ /petroleum ether) to afford the expected carbamate (5.9 g, 72%; if the product is not purified immediately after the reaction, neutralization of the residual acid is advised): TLC (50%  $Et_2O$ /petroleum ether)  $R_f = 0.2$ ; IR (NaCl,  $cm^{-1}$ ) 1750-1700, C=O, 1610, C=C; NMR ( $CDCl_3$ , ppm) 7.26 (d, 2H, 8.5), 6.81 (d, 2H, 8.5), 5.32 (br s, 1H), 5.05 (s, 1H), 4.90 (s, 1H), 4.75-4.55 (two br s, <2H), 4.41 (s, 2H), 4.21 (br s, 4H), 3.90 (s, 2H), 3.80 (s, 3H), 2.23 (m, 2H), 2.14 (m, 2H), 1.85 (br s); molecular ion calcd for  $C_{25}H_{35}N_2O_6$  (M + H) 459.2497, found 459.2482.

**2,3-Diaza-7-[4'-[[4-methoxybenzyl]oxy]methyl]pent-4'-enylidene]bicyclo[2.2.1]hept-2-ene.** The above carbamate (5.9 g, 12.9 mmol) was dissolved in THF (30 mL), and a solution of KOH in  $EtOH$  (2.0 M, 100 mL) was added. The mixture was stirred at reflux for 1.5 h and then placed in an ice-water bath.  $K_3Fe(CN)_6$  (12.7 g, 38.7 mmol) was dissolved in water (50 mL) and then added from a dropping funnel to the stirring solution over 15 min. After 1.0 h, the reaction mixture was transferred to a flask and  $Et_2O$  (200 mL) was added. While the mixture was stirred at ambient temperature, water was added until the layers became homogenous, whereupon the NaCl was added until the aqueous layer became saturated. The organic portion was separated and the aqueous portion extracted with  $Et_2O$  ( $3 \times 100$  mL). The organic layers were combined, washed with brine, dried, and concentrated *in vacuo*. The residue was chromatographed (25%-50%  $Et_2O$ /petroleum ether) to afford the title diazene (3.34 g, 83%): IR (NaCl, neat,  $cm^{-1}$ ) 1650 and 1610, C=C; NMR ( $CDCl_3$ , ppm) 7.26 (d, 2H,  $J = 8.5$ ), 6.88 (d, 2H,  $J = 8.5$ ), 5.33 (d, 1H,  $J = 2$ ), 5.11-5.08 (m, 2H), 5.04 (s, 1H), 4.87 (s, 1H), 4.40 (s, 2H), 3.89 (s, 2H), 3.80 (s, 3H), 2.15-2.07 (m, 4H),

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(10) Stone, K. J.; Little, R. D. *J. Org. Chem.* 1984, 49, 1849.

1.64–1.54 (m, 2H), 1.08 (d, 2H,  $J = 8$ );  $^{13}\text{C}$  NMR (APT) positive signals 159.10, 145.00, 144.85, 130.21, 112.41, 72.58, 71.57, 32.74, 27.06, 21.40, 20.99; negative signals 129.21, 116.64, 113.69, 76.73, 72.49, 55.17; molecular ion calcd for  $\text{C}_{19}\text{H}_{24}\text{O}_2$  ( $M - \text{N}_2$ ) 284.1777, found 284.1748.

**2,3-Diaza-7-[4'-(hydroxymethyl)pent-4'-enylidene]bicyclo[2.2.1]hept-2-ene.** A solution of the diazene prepared as described above (3.07 g, 9.8 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL) containing water (1.5 mL), and the resulting stirred solution was cooled in an ice–water bath. Dicyanodichlorobenzoquinone (DDQ, 2.45 g, 10.8 mmol) was added dropwise in  $\text{CH}_2\text{Cl}_2$  (10 mL). The reaction mixture was allowed to warm to ambient temperature. When complete (TLC), a solution of  $\text{NaHCO}_3$  (30 mL, 50% satd) was added and the aqueous portion extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 30$  mL). The organic layers were combined, washed with brine, dried over  $\text{MgSO}_4$ , and concentrated *in vacuo*. Chromatography (50% to 75%  $\text{Et}_2\text{O}$ /petroleum ether) provided the desired diazene alcohol (1.71 g, 91%): TLC (75%  $\text{Et}_2\text{O}$ /petroleum ether),  $R_f = 0.15$ ; IR (NaCl, neat,  $\text{cm}^{-1}$ ) 3400, OH, 1650, C=C, 900, =CH; NMR ( $\text{CDCl}_3$ , ppm) 5.38 (s, 1H), 5.13–5.10 (m, 2H), 5.05 (s, 1H), 4.83 (s, 1H), 4.03 (s, 2H), 2.20–2.07 (m, 4H), 1.91 (br s, 1H), 1.64 (dd, 2H,  $J = 2$  and 10), 1.10 (d, 2H,  $J = 10$ );  $^{13}\text{C}$  NMR (APT) positive signals 147.62, 145.10, 110.10, 65.69, 32.47, 27.20, 21.39, 21.04; negative signals 116.61, 76.71, 72.59; molecular ion calcd for  $\text{C}_{11}\text{H}_{16}\text{O}$  ( $M - \text{N}_2$ ) 164.1202, found 164.1213.

**2,3-Diaza-7-(4'-formylpent-4'-enylidene)bicyclo[2.2.1]hept-2-ene (1).** Standard Swern oxidation conditions and the following reagent quantities were used:<sup>11</sup> oxalyl chloride (2 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL); DMSO (0.3 mL, 4.2 mmol); 0.267 g (1.4 mmol) of alcohol added in  $\text{CH}_2\text{Cl}_2$  solution ( $\approx 5$  mL); TEA (1.4 mL, 10 mmol). The solvent was removed *in vacuo* and the residue chromatographed (50%  $\text{Et}_2\text{O}$ /petroleum ether) to afford aldehyde 1 (0.19 g, 72%): TLC (50%  $\text{Et}_2\text{O}$ /petroleum ether)  $R_f = 0.2$ ; IR (NaCl, neat,  $\text{cm}^{-1}$ ) 2850 and 2700, Fermi aldehyde bands, 1680, C=O; NMR ( $\text{CDCl}_3$ , ppm) 9.52 (s, 1H), 6.20 (s, 1H), 6.01 (s, 1H), 5.30 (d, 1H,  $J = 2$  Hz), 5.10–5.06 (m, 2H), 2.32–2.23 (m, 2H), 2.15 (app q, 2H,  $J = 7.5$  Hz), 1.66–1.56 (m, 2H), 1.14–1.06 (m, 2H);  $^{13}\text{C}$  NMR (APT, ppm) positive signals 148.48, 145.62, 134.63, 27.56, 26.95, 21.16, 20.83; negative signals 194.07, 115.68, 76.45, 72.26; molecular ion calcd for  $\text{C}_{11}\text{H}_{14}\text{O}$  ( $M - \text{N}_2$ ) 162.1045, found 162.1056.

**Thermolysis of 1. Formation of (1R\*, 6R\*, 8R\*)-8-formyltricyclo[6.2.0.0<sup>2,4</sup>]dec-2-ene (2a) and 1-Ethenyl-5-(2'-formyl-2'-propenyl)cyclopentene (3).** In a typical case, diazene 1 (0.05 g, 0.263 mmol) was dissolved in THF (250 mL; freshly distilled from Na/benzophenone ketyl). The solution was degassed with argon for at least 1.5 h and then refluxed under argon for 3.0 h. Analysis (TLC, GC,  $^1\text{H}$  NMR) of the volatile crude products revealed the exclusive formation of aldehydes 2a and 3 (1.6–1.65:1 ratio). The products were separated and isolated by chromatography over silica gel using 2–10%  $\text{Et}_2\text{O}$ /petroleum ether as the eluent; the combined isolated yields ranged from 66 to 85%.

For 2a: IR (NaCl, neat,  $\text{cm}^{-1}$ ) 2860 and 2700, Fermi bands, 1705, C=O; NMR ( $\text{CDCl}_3$ , ppm) 9.61 (s, 1H), 5.31 (s, 1H), 3.64 (br t, 1H,  $J = 7.5$ ), 3.21 (dd, 1H,  $J = 3$  and 9), 2.7–2.5 (m, 3H), 2.35–2.2 (m, 2H), 1.86–1.80 (m, 2H), 1.73–1.67 (m, 1H), 1.59–1.51 (m, 1H), 1.46 (app t, 1H,  $J = 11$ );  $^{13}\text{C}$  NMR (APT, ppm) positive signals 154.06, 63.34, 39.14, 37.92, 31.79, 22.33, 21.63; negative signals 202.30, 119.80, 50.35, 39.11; molecular ion calcd for  $\text{C}_{11}\text{H}_{14}\text{O}$  162.1045, found 162.1032.

For 3: IR (NaCl, neat,  $\text{cm}^{-1}$ ) 2840 and 2700, Fermi bands, 1680, C=O; 1630, C=C; 910, =CH; NMR ( $\text{CDCl}_3$ , ppm) 9.57 (s, 1H), 6.46 (dd, 1H,  $J = 10.5$  and 17.5), 6.28 (s, 1H), 6.05 (s, 1H), 5.71 (s, 1H), 5.38 (d, 1H,  $J = 17.5$ ), 5.12 (d, 1H,  $J = 10.5$ ), 3.01 (app t, 1H,  $J = 10$ ), 2.73 (d, 1H,  $J = 14$ ), 2.39 (app pentet, 1H,  $J = 8.5$ ), 2.27 (app dd, 1H,  $J = 9$  and 17.5), 1.97–1.86 (m, 2H), 1.63 (m, 1H,  $J = 2$  and  $\approx 10$ );  $^{13}\text{C}$  NMR (APT, ppm) positive signals 149.29, 145.99, 135.12, 114.46, 31.26, 30.52, 28.92; negative signals 194.81, 132.14, 130.92, 41.59; molecular ion calcd for  $\text{C}_{11}\text{H}_{14}\text{O}$  162.1045, found 162.1029.

For alcohol 2b: IR (NaCl, neat,  $\text{cm}^{-1}$ ) 3350, 3040, 2940, 2840, 1660, 1440, 1030, 800; NMR 5.22 (s, 1H), 3.63 (s, 2H), 3.52 (m, 1H), 2.78 (dd, 1H,  $J = 3$  and 9), 2.66–2.59 (m, 1H), 2.55–2.48 (m, 1H), 2.26–2.18 (m, 2H), 1.97 (app hexet, 1H,  $J = 6$ ), 1.88 (m, 1H), 1.73 (dd, 1H,  $J = 7.5$  and 11), 1.61 (m, 1H), 1.49–1.41 (m, 1H), 1.02 (t, 1H,  $J = 11$ ); molecular ion calcd for  $\text{C}_{11}\text{H}_{16}\text{O}$  164.1202, found 164.1201.

**Procedure for Oxygen Quenching.**<sup>1,12</sup> A 2 mM solution of diazene 1 (23 mg, 0.12 mmol) and  $\text{C}_{22}\text{H}_{46}$  (internal standard, 50 mg, 0.16 mmol) in 2-methyltetrahydrofuran (freshly distilled from Na/benzophenone ketyl, 60 mL) was divided into two portions. One portion was degassed with argon and refluxed for 3.0 h.

The second portion was stirred at ambient temperature while a stream of oxygen gas was bubbled through it. After at least 2.0 h, the reaction vessel was placed in an oil bath heated to 60–65 °C. Oxygen gas was continually bubbled through through the solution while it was stirred in the oil bath. When no trace of diazene could be observed by TLC, aliquots from both reactions were examined by GC. The first reaction exclusively produced the aldehydes 2a and 1 in the expected 1.65/1 ratio. The second produced none of trienal 3, only aldehyde 2a and other uncharacterized products presumed to be oxygen-derived products.<sup>12</sup> In a control experiment, the product mixture from the first reaction was submitted to the reaction conditions of the second reaction for 4.0 h. No appreciable decomposition (<5%) of either product was observed.

**Acknowledgment.** We are most grateful to the National Cancer Institute of the National Institutes of Health for their support of this research.

**Supplementary Material Available:** Spectral data and NMR spectra ( $^1\text{H}$  and  $^{13}\text{C}$ -APT) for 1, 2a, and 3 (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(12) Little, R. D.; Losinski-Dang, L.; Venegas, M. G.; Merlic, C. *Tetrahedron Lett.* 1983, 23, 4499.