(2-Vinylcyclopropyl)carbenes. More Stepwise Mechanisms for Ring-Expansion

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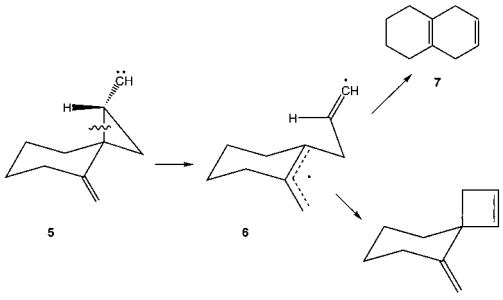
Received April 19, 1999

Abstract: A simple vinyl group is sufficient to induce a stepwise mechanism for the ring expansion of cyclopropylcarbenes.

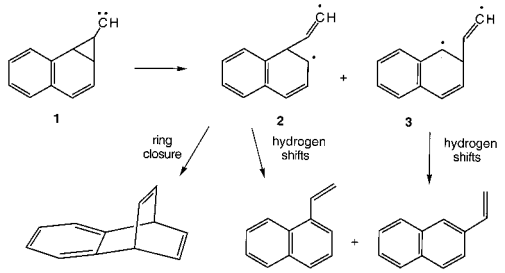
We recently showed that the naphthofused cyclopropylcarbene **1** rearranged, inter alia, to 2- and 3-vinylnaphthalene[1] and suggested that this observation was most easily rationalized through the intervention of diradicals **2** and **3**. We interpreted the presence of these intermediates to mean that the carbene was rearranging in a stepwise fashion, a most unusual event for a singlet carbene (Scheme 1).[2] In a sense, this work validated the mechanism proposed nearly 30 years ago by Reich and Scott for related cyclopropylcarbene rearrangements (Scheme 2).[3]

Why was such a validation necessary? Why could the Reich/Scott mechanism of Scheme 2 not stand on its own feet? The problem was that there was no solid evidence that diradicals analogous to **2** and **3**, and the ones implied in the Reich/Scott work, were involved in reactions of simple cyclopropylcarbenes[4] or, most important, in reactions of vinyl-substituted cyclopropylcarbenes.[5] Although it might be argued in Cummins' work on **1**[1] that substantially more resonance stabilization than that from a single vinyl group was afforded the delocalized portion of the diradical, it is harder to make that case in the Reich/Scott work.[2] Here, the double bonds in the tub-like cyclooctatriene system are not well-disposed for stabilizing the transition state for bond breaking in the three-membered ring. Moreover, we suspected that the absence of products indicating stepwise decomposition of the carbene owed more to geometry than to electronic factors. Thus, in Sasaki et al.'s typical example,[5] there would be an energetic advantage to having the vinyl group in an extended position rather than coiled under the three-membered ring. In that extended form, a transoid allyl radical (**4**) must be formed, and no easy closure to a rearranged cycohexadiene is available (Scheme 3). We reckoned that if a carbene could be generated in which a cisoid allyl radical was obligatory, the "missing" rearranged products would be found. The carbene we sought was **5**, in which stepwise opening would lead to diradical **6** and, ultimately, to **7**.

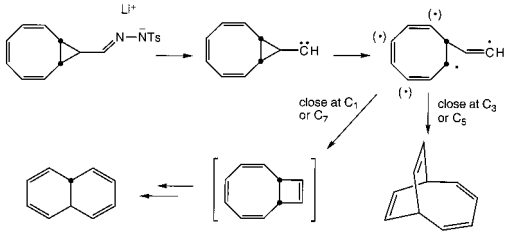


The synthesis of our test molecule began from 1,2-dimethylenecyclohexane.[6] Cyclopropanation with ethyl diazoacetate,

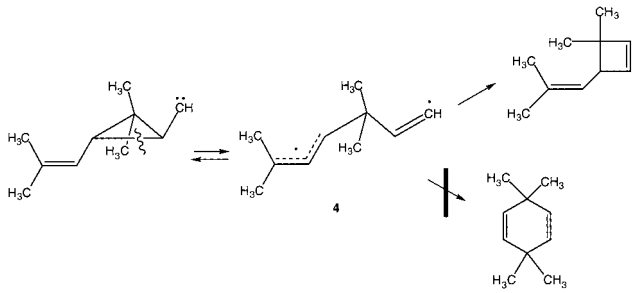
Scheme 1. Cummins' Mechanism for Rearrangement of Cyclopropylcarbene **1**



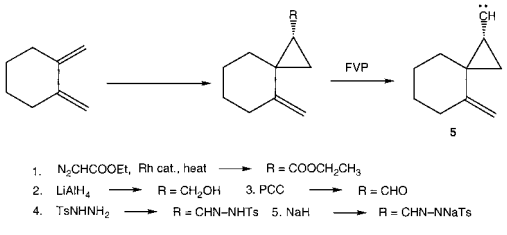
Scheme 2. Reich and Scott's Mechanism for Cyclopropylcarbene Rearrangements



Scheme 3. Closure of the Trans Diradical to a Six-Membered Ring Is Difficult



Scheme 4. Generation of Carbene **5**



followed by reduction to the alcohol, and reoxidation to the

(1) Cummins, J. M.; Porter, T. A.; Jones, M., Jr. *J. Am. Chem. Soc*. **1998**, *120*, 6473.

(2) Unusual, but not quite unprecedented: Berdick, T. E.; Levin, R. H.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc*. **1973**, *95*, 5087.

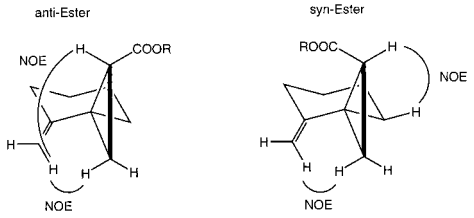
10.1021/ja991254r CCC: $18.00
Published on Web 08/06/1999

Table 1. Product Formation from the Anti Carbene as a Function of Temperature

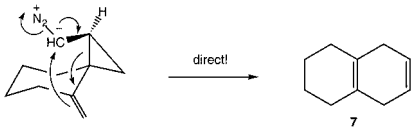
temp (°C)	% **7**	% **8**	% **9**	% **10**	% **11**	%**12**
340	61	12	1	19	7	0
400	56	17	1	17	9	0
460	57	12	3	27	1	0
520	54	11	8	26	1	0
580	52	13	11	23	1	
25 (*hν*)	14	0	9	5	1	71

aldehyde was conventional, as was formation of the tosylhydrazone and its sodium salt (Scheme 4).

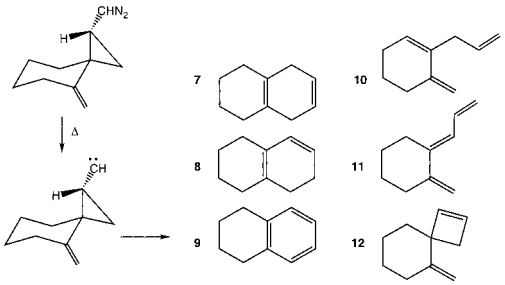
In the cyclopropanation, two diastereomers are formed and were easily separated by column chromatography. Not so easy, however, was the identification of the diastereomers. Details can be found in the Experimental Section, but the critical differentiation rests on the observation of nuclear Overhauser effects between the hydrogens shown below. It was important



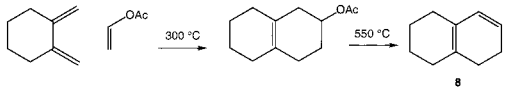
that we carry forward the anti diastereomer to the carbene stage because only it would be immune to criticism that direct interaction between the syn diazo compound or carbene and the double bond might be leading to rearranged product. An example of the mischief possible in the syn series is shown below. Diene **7** could be formed by a direct rearrangement of the syn diazo compound. As it was exactly formation of **7** that we expected to see from a stepwise rearrangement of the carbene, it was critical that we use the anti series.



Decomposition of the anti diazo compound, generated in a flowing system through heating of the anti tosylhydrazone salt, led to a mixture of products **7**−**11** that was largely independent of temperature over the range 340−580 °C (Table 1). The major product throughout the temperature range is **7**, exactly as expected if a diradical were involved.



Scheme 5. Synthesis of **8**



Scheme 6. An Alternative Mechanism for the Formation of **7**

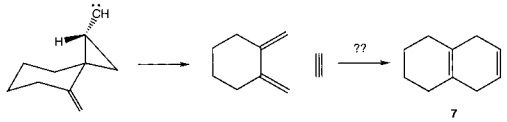


Table 2. Products from the Syn Carbene as a Function of Temperature

temp (°C)	% **7**	% **8**	% **9**	% **10**	% **11**	% **12**
460	59	15	7	14	5	0
520	56	20	8	12	4	0

Compounds **7** and **9** were compared to commercial samples, and compounds **11** and **12** were known from the work of Paul and Gajewski.[7] Compound **8** was also reported by Paul and Gajewski[7] but was synthesized independently as shown in Scheme 5. Compound **10** is new but was readily identified from its precise mass spectrum and ^{1}H NMR spectrum.

One would surely also expect the formation of **12**, either as another recombination product from the diradical intermediate or from direct ring expansion of either the carbene or diazo compound. Indeed, when the reaction is carried out photolytically at low temperature, **12** does appear as the major product of the reaction. Identification was by mass spectrometry and comparison of its ^{1}H NMR spectra with that of the authentic compound.[7] Paul and Gajewski's investigation of the thermal chemistry of **12** came to the unsurprising conclusion that **12** rearranged above 100 °C to both **8** and **11** but not to **7**. A control experiment showed that tetralin, **9**, is formed from **8** under our conditions. So the major surmise of this work is borne out: cyclohexadienes should be formed from (2-vinylcyclopropyl)-carbenes provided only that the diradical intermediate can be formed in the cisoid arrangement necessary for closure to the six-membered ring. The formation of **7** in such large amounts confirms the stepwise nature of these carbene reactions.

Of course other mechanisms must be considered. Much fragmentation to 1,2-dimethylenecyclohexane occurs in this reaction, as expected. Acetylene must be the other product. Is it reasonable to expect the major product, **7**, to be formed by a Diels−Alder reaction between these two products (Scheme 6)? Surely not. At 25 °C, the Diels−Alder reaction between acetylene and the diene will be extraordinarily slow,[8] and even at 550 °C it is not credible that these two molecules will encounter each other enough in the gas phase to form the major product.

The syn diazo compound also leads to the same products, but here the possibility of direct reaction from the diazo compound makes the presence of **7** mechanistically uninformative (Table 2). The general correspondence between the products of the syn and anti systems makes intervention of the same intermediates, presumably the carbene and diradical **6**, likely, however. Only one substantive difference appears in the product distributions from the two carbenes, and it may be mechanisti-

(3) Jones, M., Jr.; Reich, S. D.; Scott, L. T. *J. Am. Chem. Soc*. **1970**, *92*, 3118.

(4) For a review of cyclopropylcarbene chemistry, see: Arct, J.; Brinker, U. H. In *Methoden der Organische Chemie (Houben-Weyl)*; Regitz, M., Ed.; G.Thieme Verlag: Stutttgart, 1989; Vol. E19b, pp 337−375.

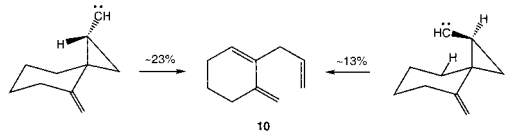
(5) Sasaki, T.; Eguchi, S.; Ohno, M.; Umemura, T. *J. Org. Chem.* **1973**, *38*, 4095.

(6) Baily, W. J.; Golden, H. R. *J. Am. Chem. Soc.* **1953**, *75*, 4780.

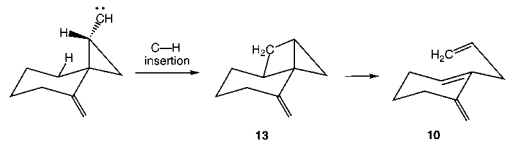
(7) Paul, G. C.; Gajewski, J. J. *J. Org. Chem*. **1992**, *57*, 1970.

(8) Plate, A. F.; Pryanishnikova, M. A. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **1956**, 741.

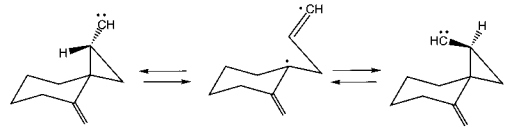
cally significant: there is only about half the amount of **10** formed from the syn starting material as there is from the anti material.



How is **10** formed? We suggest that carbon−hydrogen insertion leads to **13** from which **10** should be easily available at these temperatures. But the carbon−hydrogen bond necessary



for the formation of **13**, and hence, **10**, is well out of range for the syn carbene. Yet **10** is formed, albeit in reduced amount. Perhaps diradical formation is reversible. If so, this process provides an epimerization pathway for the two carbenes and therefore a possible route to formation of **10** from the syn carbene.



Two qualifications attend the conclusions of this work. First, we must make the reasonable assumption that decomposition of the intermediate alkyl diazo compounds is faster than epimerization of the anti diazo compound to the syn diazo compound. Second, although it would seem that the presence of a single vinyl group is sufficient to make diradical formation possible, of course our results do not speak to the question of the reaction mechanism of nonactivated cyclopropylcarbenes. Direct irradiation of a series of stereolabeled cyclopropyl diazo compounds was shown long ago to lead to complete retention of stereochemistry in both the ring-expanded and fragmented products.[9] However, we now know that cyclobutene formation from cyclopropyl diazo compounds is entirely,[10] or predominately,[10,11] a reaction of the diazo compound and not the carbene. We are planning to reinvestigate the stereochemistry of the ring expansion reaction, but there is one experiment lurking in the literature that makes it probable that no stereochemical scrambling will be found. In the photolysis of cyclopropyl diazo compounds mentioned earlier,[9] both the direct and photosensitized photolyses led to retention of stereochemistry in the products. The direct photolyses are uninformitive mechanistically, but the photosensitized reactions do tell us much. In the sensitized reactions, triplet diazo compound leads to triplet carbene, which has little available intramolecular chemistry. Intersystem crossing forms the singlet, which does "real" singlet carbene chemistry, and leads to ring expansion. Thus, the observation of retention in the sensitized reactions gives us an indirect peek at the chemistry of the singlet carbenes.

Although a vinyl-substituted cyclopropylcarbene has not been examined, for the parent cyclopropylcarbene a diradical intermediate emerges as competitive with concerted fragmentation from the trans conformation of the carbene, in which ring expansion is slow.[12] At this point it would appear that the vinyl group is both necessary and sufficient for the two-step mechanism to undercut the one-step process energetically.

Experimental Section

General. Photolysis was carried out with a 450-W medium-pressure mercury arc (Hanovia lamp). Routine ^{1}H NMR spectra were obtained on either a GE/Tecmag QE-300 (300 MHz) or a JEOL/Tecmag GSX-270 (270 MHz) spectrometer. ^{1}H/^{13}C 1D and 2D spectra for the anti and syn esters were acquired at 600/150 MHz on a Varian Unity/INOVA instrument. Gas chromatographic/mass spectrometric analyses were performed on a Hewlett-Packard 5890/5971 Series II gas chromatograph/mass spectrometer with a HP-1701 capillary column (30 m × 0.25 mm id, 0.25 mm film thickness). Preparative gas chromatography was performed on a Gow-Mac 580 gas chromatograph with an aluminum column (6 ft × $^1/_4$ in) packed with 10% OV-101 on Chromosorb WHP. Precise masses were measured on a KRATOS MS50 RFA high-resolution mass spectrometer. GC/FTIR measurements were made on a Hewlett-Packard HP 5898 gas chromatograph (30 m × 0.32 mm id, 0.5 mm film thickness) with a Restek rtx-1 column connected to a Nicolet 730 FTIR spectrometer. Ethyl diazoacetate, *p*-toluenesulfonylhydrazide, PCC, NaH, *cis*-1,2-cyclohexanedicarboxylic anhydride, acetic anhydride, rhodium(II) acetate dimer, vinyl acetate, and tetralin were acquired from Aldrich Chemical Co. 1,2,3,4,5,8-Hexahydronaphthalene was acquired from Chemsampco Corp. Solvents (Et_2O, CH_2Cl_2, THF) were dried and distilled prior to use.

***cis*-1,2-Cyclohexanedimethanol.** To 3.5 L of anhydrous THF was added 57 g of $LiAlH_4$ (1.5 mol) with vigorous stirring. To this mixture was added 190.4 g (1.24 mol) of *cis*-1,2-cyclohexanedicarboxylic anhydride dissolved in 500 mL of THF dropwise over 1 h. The resulting suspension was then maintained at reflux for 3 h with a heating mantle. After this time, heating was ceased and 400 mL of a freshly prepared saturated aqueous Na_2SO_4 solution was cautiously added dropwise. The resultant white lithium salts were removed by suction filtration and washed with 100 mL of ether. The combined filtrates were stripped of solvent to give 156 g (88%) of a colorless, viscous oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (m, 8H), 1.94 (m, 2H), 3.68 (m, 4H).

Diacetate of *cis*-1,2-Cyclohexanedimethanol. *cis*-1,2-Cyclohexanedimethanol (156 g, 1.1 mol) and 1 mL of pyridine were heated to 120 °C. Over a period of 30 min, 330 g of acetic anhydride (3.2 mol) was added to the glycol, and the mixture was stirred for 45 min. The acetic acid and acetic anhydride were removed by vacuum distillation. The residue was distilled under reduced pressure to give 235 g (95%) of the diacetate as a clear viscous oil, bp 31−40 °C (3 Torr): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40−1.56 (m, 10H), 2.06 (m, 6H), 4.05 (m, 4H).

1,2-Dimethylenecyclohexane.[6] At a rate of approximately 0.5 g per min, 230 g (1.0 mol) of the diacetate of *cis*-1,2-cyclohexanedimethanol was dropped via an addition funnel into a 12 mm × 25 cm Pyrex column packed to a depth of 17 cm with 3 mm Pyrex beads, and the solution was heated externally to 650 °C by a tube furnace. The pyrolysate vapor was conducted into a cooled (−78 °C) collection flask by a stream of argon, which was introduced through the addition funnel (sealed to the Pyrex column with Parafilm). A drying tube outlet was connected to the receiving flask as a necessary outlet for excess pressure. The pyrolysis products were washed with 3 × 100 mL of distilled water to remove acetic acid and dried over Na_2SO_4. Analysis by GC/MS indicated that approximately 50% of the product was monoacetate. The residue was distilled under reduced pressure to give 30 g (28%) of pure 1,2-dimethylenecyclohexane, bp 30−35 °C (30 Torr). The residue in the still pot was repyrolyzed and distilled to give an additional 25.2 g (22%) of pure product. The portions were combined to give 55.2 g (50%) of 1,2-dimethylenecyclohexane as a free-flowing colorless

(9) Gallucci, R. R.; Jones, M., Jr. *J. Am. Chem. Soc*. **1976**, *98*, 7704.
(10) Huang, H.; Platz, M. S. *Tetrahedron Lett.* **1996**, *37*, 8337; *J. Am. Chem. Soc*. **1998**, *120*, 5990.
(11) Thamattoor, D. M.; Jones, M., Jr.; Pan, W.; Shevlin, P. B. *Tetrahedron Lett.* **1996**, *37*, 8333.
(12) Schoeller, W. W. *J. Org. Chem*. **1980**, *45*, 2161. Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc*. **1995**, *117*, 3685.

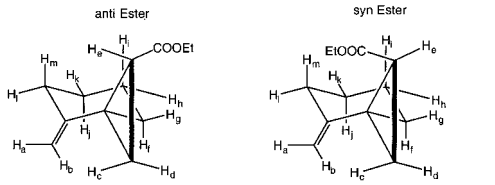
liquid: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.66 (m, 4H), 2.28 (m, 4H), 4.66 (m, 2H), 4.95 (m, 2H).

2-Acetoxy-1,2,3,4,5,6,7,8-octahydronaphthalene. A sample of 4 g of 1,2-dimethylenecyclohexane (37 mmol) and a large excess (40 mL) of vinyl acetate was placed in a 100 mL bomb. The mixture was heated at 300 °C for 2 h and allowed to cool to ambient temperature. The reaction products were concentrated under reduced pressure to remove excess vinyl acetate. A yellow oil (4.4 g, 61%) was recovered and analyzed by GC/MS. This product was used in the next step without further purification.

1,2,3,4,5,6-Hexahydronaphthalene.[13] At a rate of approximately 0.25 g per min, 750 mg of the acetate synthesized in the previous step was dropped via an addition funnel into a 12 mm × 25 cm Pyrex column packed to a depth of 17 cm with 3 mm Pyrex beads and heated externally to 550 ± 15 °C by a tube furnace. The pyrolysate vapor was conducted into a cooled (−78 °C) collection flask by a stream of argon, which was introduced through the addition funnel (sealed to the Pyrex column with Parafilm). A drying tube outlet was connected to the receiving flask as a necessary outlet for excess pressure. The pyrolysis products were washed with 3 × 15 mL of distilled water to remove acetic acid and dried over Na_2SO_4. The major product was purified by preparative gas chromatography; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.57 (m, 1H), 1.66 (m, 4H), 1.85 (m, 1H), 2.03 (m, 4H), 2.17 (m, 2H), 5.71 (m, 2H). This spectrum matched spectra from the literature.[13]

***anti*- and *syn*-7-Ethoxycarbonyl-5-methylenespiro[2.5]octane.** To 20.0 g of 1,2-dimethylenecyclohexane (0.19 mol) and 60 mg of rhodium(II) acetate dimer (0.14 mmol) suspended in 100 mL of Et_2O was added dropwise 21.1 g of ethyl diazoacetate (0.19 mol) dissolved in 70 mL of Et_2O over a period of 9 h. The crude products were passed through a silica gel column and washed with 3 × 50 mL of CH_2Cl_2. This material was concentrated to dryness, yielding 34.1 g of a clear oil. Analysis by GC/MS indicated the presence of two diastereomers with the expected molecular weight of 194. These compounds were separated on a silica gel column (90/10 hexanes/ether). A total of 15 g of the more mobile ester was collected as a colorless oil: ^{1}H NMR (600 MHz, benzene-d_6) δ 1.02 (t, 3H), 1.08 (dd, 1H), 1.20 (dd, 1H), 1.32−1.60 (m, 4 H), 1.63 (dd, 1 H), 1.68 (m, 1H), 1.92 (m, 1H), 2.12 (m, 2H), 4.02 (m, 2H), 4.52 (s, 1H), 4.56 (s, 1H); ^{13}C NMR (150 MHz, benzene-d_6) δ 171.9, 151.6, 106.2, 60.6, 35.8, 35.3, 30.7, 28.6, 26.9, 26.2, 18.9, 14.8. A total of 3 g of the less mobile ester was collected as a colorless oil: ^{1}H NMR (600 MHz, benzene-d_6) δ 0.58 (dd, 1H), 0.72 (m, 1H), 0.98 (t, 3H), 1.28 (m, 1H), 1.50 (m, 2H), 1.54 (dd, 1H), 1.64 (m, 3H), 1.90 (m, 1H), 2.22 (m, 1H), 3.93 (q, 2H), 4.82 (s, 1H), 4.87 (s, 1H); ^{13}C NMR (150 MHz, benzene-d_6) δ 170.6, 145.8, 110.1, 60.3, 39.2, 36.0, 35.9, 28.7, 28.6, 26.1, 17.6, 14.9. The structures and relative geometries of these two products were confirmed by means of carbon/hydrogen 2D correlations and selective proton irradiations. The more mobile ester was assigned the anti stereochemistry, and the less mobile ester was assigned the syn stereochemistry through 1D NOE difference spectroscopy. HRMS (EI) calcd for the anti isomer: $C_{12}H_{18}O_2$, 194.13068; found 194.13206. HRMS (EI) calcd for the syn isomer: $C_{12}H_{18}O_2$, 194.13068; found 194.13021.

Stereochemistry of *anti*- and *syn*-7-Ethoxycarbonyl-5-methylenespiro[2.5]octane. One-dimensional nuclear Overhauser enhancement difference spectroscopy (NOEDS)[14] at 600 MHz was used to prove the structure of the anti and syn esters (labeling as shown below). For these experiments, selective (ca. 35 Hz) irradiation was applied for 5 s, followed by a 10 ms recovery delay, a 45° read pulse, and data acquisition. Successive on-resonance experiments and one off-resonance experiment for reference were collected in a supercycle for long-time averaging. Difference spectra were calculated and integrated using standard tools of the Vnmr software (Varian). The observed NOE data are listed below. Additional information was provided by comparative assignment of the carbon resonances, using gradient-selected ^{13}C,^{1}H-HSQC spectra.[15]



Irradiate at:	NOE Response	Rel. %	Irradiate at:	NOE Response	Rel. %
H_a	H_b	(3.4)	H_a	H_b	12.0
	H_i and H_m	1.9		H_i	3.0
H_b	H_a	(4.8)	H_b	H_a	12.0
	H_c	5.4		H_c	4.8
	H_d	−0.6		H_d	−0.4
	H_e	3.8			
H_c	H_d	16.0	H_d	H_c	17.6
	H_e	4.0		H_e	3.5
	H_b	4.7		H_g	1.2
				H_b	−0.4

***anti*-7-Hydroxymethyl-5-methylenespiro[2.5]octane**. A sample of the anti ester (0.960 g, 4.95 mmol, 1 equiv) was dissolved in 8 mL of anhydrous Et_2O and added dropwise to a mixture of $LiAlH_4$ (0.282 g, 7.42 mmol, 1.5 equiv) in 9 mL of refluxing anhydrous Et_2O over 1 h. The reaction was followed by TLC (80/20 hexanes/Et_2O). Reflux was maintained for another 1.5 h, at which time 10% NH_4Cl (30 mL) was carefully added to quench the reaction. The mixture was filtered to remove the product, which was washed with excess ether and CH_2Cl_2. The aqueous layer was extracted with 50 mL of Et_2O, and the combined organic layers were dried over Na_2SO_4. A total of 583 mg (78%) of anti alcohol was recovered as a colorless oil, which was used in the subsequent step without further purification: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.29 (m, 1H), 0.86 (m, 1H), 1.24 (m, 2H), 1.59 (m, 7H), 2.24 (m, 1H), 3.71 (m, 2H), 4.56 (s, 1H), 4.60 (s, 1H); HRMS (EI) calcd for $C_{10}H_{16}O$ 152.12012, found 152.12111.

***syn*-7-Hydroxymethyl-5-methylenespiro[2.5]octane**. A sample of the syn ester (3 g, 15.5 mmol) was dissolved in anhydrous Et_2O (20 mL) and added dropwise to a mixture of $LiAlH_4$ (1.02 g, 26.8 mmol) in 25 mL of refluxing anhydrous Et_2O over 1.5 h. The reaction was followed by TLC (80/20 hexanes/Et_2O). Reflux was maintained for another 1.25 h, at which time 6 mL of 10% NH_4Cl was carefully added to quench the reaction. The mixture was filtered to remove the product, which was washed with excess ether and CH_2Cl_2. The aqueous layer was extracted with 10 mL of Et_2O, and the combined organic layers were dried over Na_2SO_4. The organic layers were concentrated to give 2.2 g (93%) of syn alcohol as a colorless oil, which was used in the subsequent step without further purification: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.51 (m, 1H), 0.71 (m, 1H), 0.82−2.10 (m, 9H), 2.23 (m, 1H), 3.66 (m, 2H), 4.59 (s, 1H), 4.79 (s, 1H); HRMS (EI) calcd for $C_{10}H_{16}O$ 152.12012, found 152.11918.

***anti*-5-Methylenespiro[2.5]octane-7-carboxaldehyde.** A sample of the anti alcohol (580 mg, 3.8 mmol, 1 equiv) dissolved in 10 mL of dry CH_2Cl_2 was rapidly charged into a heterogeneous mixture of PCC (1.23 g, 5.7 mmol, 1.5 equiv) in 12 mL of dry CH_2Cl_2. The mixture immediately turned black. The reaction was followed by TLC (85/15 hexanes/Et_2O) and diluted with 3 × 5 mL of Et_2O upon completion (1 h). The crude product was filtered through Flourisil and concentrated under reduced pressure to yield 443 mg (77%) of a pale yellow oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.29−2.24 (m, 10H), 2.32 (m, 1H), 4.64 (s, 1H), 4.68 (s, 1H), 9.54 (d, 1H, J = 4.8 Hz); HRMS (EI) calcd for $C_{10}H_{13}O^+$ (the acylium ion) 149.09664, found 149.09687.

***syn*-5-Methylenespiro[2.5]octane-7-carboxaldehyde.** A sample of the syn alcohol (2 g, 13.2 mmol, 1 equiv) dissolved in 40 mL of dry CH_2Cl_2 was rapidly charged into a heterogeneous mixture of PCC (4.3 g, 19.9 mmol, 1.5 equiv) in 50 mL of dry CH_2Cl_2. The mixture immediately turned black. The reaction was followed by TLC (85/15 hexanes/Et_2O) and diluted with 3 × 20 mL of Et_2O upon completion (2 h). The crude product was filtered through Flourisil and concentrated under reduced pressure to yield 1.5 g (76%) of a pale yellow oil. Analysis of this product by ^{1}H NMR indicated that the desired syn

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aldehyde was contaminated with anti aldehyde. The mixture was separated on a silica gel column (90/10 hexanes/Et_2O). After subsequent TLC analysis and product concentration, 291 mg of syn aldehyde was recovered as a colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94−1.85 (m, 10H), 2.28 (m, 1H), 4.75 (s, 1H), 4.77 (s, 1H), 8.65 (d, 1H, J = 4.9 Hz); HRMS (EI) calcd for $C_{10}H_{14}O$ 150.10447, found 150.10443.

Tosylhydrazone of *syn*-5-Methylenespiro[2.5]octane-7-carboxaldehyde. A sample of the anti aldehyde (1.0 g) dissolved in a minimal amount of EtOH was added dropwise to *p*-toluenesulfonylhydrazide (1.37 g, 1.1 equiv) in 7 mL of EtOH and 0.7 mL of glacial acetic acid with stirring at 50 °C. The heterogeneous mixture was allowed to stir for 12 h. The mixture was warmed to 70 °C and allowed to cool to room temperature. Crystallization did not ensue. Recrystallization from THF and CH_3OH was attempted without success. The sample was concentrated to dryness to yield 2.1 g (99%) of a sticky yellow paste: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.12−2.34 (m, 13H), 2.46 (s, 3H), 4.59 (m, 2H), 7.33 (m, 2H), 7.82 (m, 2H); HRMS (EI) calcd for $C_{17}H_{22}O_2N_2S$ 318.14189, found 318.13870.

Tosylhydrazone of *syn*-5-Methylenespiro[2.5]octane-7-carboxaldehyde. A sample of the syn aldehyde (291 mg) dissolved in a minimal amount of EtOH was added dropwise to *p*-toluenesulfonylhydrazide (397 mg, 1.1 equiv) in 1.5 mL of EtOH and 0.15 mL of glacial acetic acid with stirring at 50 °C. The heterogeneous mixture was allowed to stir for 15 h. The mixture was warmed to 70 °C and allowed to cool to room temperature. Crystallization did not ensue. Recrystallization from THF and CH_3OH was attempted without success. The sample was concentrated to dryness to yield 564 mg (91%) of a sticky yellow paste: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.05−2.30 (m, 13H), 2.45 (s, 3H), 4.68 (m, 2H), 7.34 (m, 2H), 7.83 (m, 2H); HRMS (EI) calcd for $C_{17}H_{22}O_2N_2S$ 318.14189, found 318.13893.

Sodium Salt of the Anti Tosylhydrazone. A solution of the anti tosylhydrazone (360 mg, 1 equiv) in a minimum amount of dry THF (2 mL) was added by syringe to NaH (30 mg, 1.1 equiv) in a small flask flushed with argon (with a vent for evolved H_2). After the addition, the solvent was evaporated with a stream of argon, resulting in a yellow film coating the bottom of the flask. The salt was allowed to dry for 14 h.

Sodium Salt of the Syn Tosylhydrazone. A solution of the tosylhydrazone (180 mg, 1 equiv) in a minimum amount of dry THF (1 mL) was added by syringe to NaH (15 mg, 1.1 equiv) in a small flask flushed with argon (with a vent for evolved H_2). After the addition, the solvent was evaporated with a stream of argon, resulting in a yellow film coating the bottom of the flask. The salt was allowed to dry for 17 h.

Flash Vacuum Pyrolysis of the Sodium Salt of the Anti Tosylhydrazone at 340 °C. Salt as prepared above was equilibrated at 0.005 Torr (25 min) and then heated to 120 °C to generate the diazo compound, which was led into a heated quartz tube held at 340 °C. The reaction product was condensed in a liquid nitrogen cooled trap at the end of the oven. Approximately 50% of the starting material is converted into product (by mass) in this and subsequent FVP reactions. The products were dissolved in CH_2Cl_2 (1 mL) and identified by comparison with spectra of authentic samples or from the literature. Pyrolyses at other temperatures were carried out in the same manner. New compound **10**: ^{1}H NMR (600 MHz; benzene-d_6) δ 5.85 (m, 1H), 5.61 (s,1H), 5.08 (m, 2H), 5.00 (s, 1H), 4.80 (s, 1H), 2.95 (d, 2H), 2.35 (m, 2H), 1.98 (m, 1H), 1.75 (s, 1H), 1.57 (m, 2H); HRMS (EI) calcd for $C_{10}H_{14}$ 134.10955, found 134.10885.

Flash Vacuum Pyrolysis of the Sodium Salt of the Syn Tosylhydrazone at 340 and 520 °C. The same procedure as in the reaction at 340 °C of the anti compound was used. Products were identified by means of GC/MS comparisons.

Flash Vacuum Pyrolysis of 1,2,3,4,5,8-Hexahydronaphthalene at 520 °C. 1,2,3,4,5,8-Hexahydronaphthalene was equilibrated at 0.005 Torr and immediately led into a heated quartz tube held at 520 °C. The reaction product was condensed in a liquid N_2 trap at the end of the oven. The products were dissolved in 1 mL of CH_2Cl_2 and analyzed by GC/MS.

Flash Vacuum Pyrolysis of 1,2,3,4,5,6-Hexahydronaphthalene at 520 °C. 1,2,3,4,5,6-Hexahydronaphthalene was equilibrated at 0.005 Torr and immediately led into a heated quartz tube held at 520 °C. The reaction product was condensed in a liquid N_2 trap at the end of the oven. The products were dissolved in 1 mL of CH_2Cl_2 and analyzed by GC/MS.

Photolysis of the Sodium Salt of the Anti Tosylhydrazone at 25 °C. A 300 mg sample of the anti tosylhydrazone salt was transferred under argon into a quartz tube, and 0.25 mL of CH_3OH was added. The vessel was evacuated, and the CH_3OH was evaporated as the tube walls were coated with a thin film of salt. After completely removing solvent, the sealed quartz tube was photolyzed for 8 h at 25 °C at which time the products were dissolved in pentane, filtered, concentrated, and analyzed by GC/MS and NMR spectroscopy.

Acknowledgment. We thank the National Science Foundation for generous support of this work through Grant CHE 9702823. Professor J. J. Gajewski provided spectra and helpful comments.

JA991254R