Observation of Two Characteristic Methylenecyclopropane Stereomutations in a System That also Forms Trimethylenemethane Dimers. An Experimental Connection between Putative and Directly Observed Biradicals

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Abstract: A stereospecific synthesis of 7-*syn*-deuteriomethylene-5-*exo*-methoxy-2,3-diazabicyclo[2.2.1]hept-2-ene (**20**-*8-syn-d*) from 6-bromofulvene is effected in ten steps. Irradiation of the undeuterated analogue (**20**) at 77 K in a glassy medium gives rise to a long-lived signal characteristic of the triplet state of 2-methylene-4-methoxycyclopentane-1,3-diyl. This appears to be the biradical's ground state, and a typical dilution effect on the cycloadduct composition in the reaction of the species with cyclopentadiene supports this conclusion. In the reactions of the deuterated diazene **20**-*8-syn-d* with cyclopentadiene, the deuterium label is completely scrambled. Irradiation of **20**-*8-syn-d* at −78 °C in a fluid medium gives a 3:1 mixture of *endo*- and *exo*-2-methoxy-5-deuteriomethylenebicyclo[2.1.0]pentanes (**46** and **47**). Partial but incomplete scrambling of the deuterium label is observed in both products so formed. Stereomutation by double epimerization (**47** → **46**) occurs at −60 °C; exocyclic torsion (**46**-*syn-d* → **46**-*syn-anti-d*) occurs at −40 °C; ring opening and dimer formation occur at +5 °C. Evidence for the rearrangement of the 5-methylenebicyclo[2.1.0]pentane to the bicyclo[3.1.0]hex-1-ene system above −40 °C is presented. This work shows that the characteristic structural and stereochemical rearrangements of methylenecyclopropanes can be observed in the same systems that permit direct spectroscopic observation of the biradical's triplet ground state.

Conventional mechanistic studies usually give only inferential evidence on the nature of reactive intermediates. Thus, there is a strong motivation for attempting to observe such species directly by spectroscopic means. In this way, one might provide standards of comparison for the presumably similar entities reputed to be mechanistically significant. Although one hopes to demonstrate experimentally the identity or interconvertibility of the spectroscopic and mechanistic intermediates, the conditions needed to generate the two often are so different that the desired demonstration is precluded. To the mechanistic chemist, the knowledge that his studies have inspired the observation of a new intermediate can offer but little consolation for the frustration of his larger ambition.

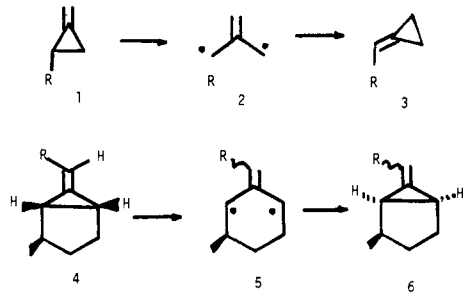
The field of thermal reactions of methylenecyclopropanes has provided a long-standing example of this problem. An extensive literature[1] usually invokes singlet trimethylenemethanes (e.g., **2** or **5**) as the key intermediates in the skeletal rearrangements (e.g., **1** → **3**) and stereomutations (e.g., **4** → **6**) observed at elevated temperatures (Scheme I).

On the other hand, trimethylenemethanes in their triplet ground states, **9** or **10**, have been generated by photodeazetation of 4-methylenepyrazolines, **7** or **8** (Scheme II), and observed directly by electron paramagnetic resonance (EPR)[1b,c,2-4] and electronic (UV-Vis)[5] spectroscopy in frozen matrices, at temperatures usually below −120 °C.

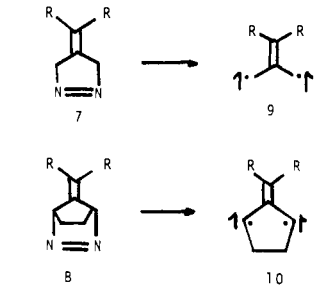
It has been clear for some time that the properties of the directly observed diazene-derived triplet trimethylenemethanes do not provide much information on the properties of the hypothetical singlet intermediates in the rearrangements. But the problem is more serious than a mere circumstantial mismatch of spin states. In some cases,[4] a singlet trimethylenemethane can be trapped as an intermediate between the bicyclic diazene **8** and the triplet trimethylenemethane. In the absence of trapping agent, spin inversion gives the more stable triplet, which ultimately forms a set of characteristic dimers. However, such spin inversions usually are not observed during the rearrangements of Scheme I.[1c] These differences in behavior might conceivably be attributed to reactions of two kinds of trimethylenemethane singlet, one that readily forms the corresponding triplet and one that does not.

A rationalization that removes the need to invoke two kinds of singlet chemistry is given in an accompanying paper.[6] For completion of the intellectual bridge between putative and directly

Scheme I. Trimethylenemethanes Postulated in Thermal Reactions



Scheme II. Trimethylenemethanes Observed Spectroscopically



(1) For reviews, see: (a) Gajewski, J. J. In "Mechanisms of Molecular Migrations", Thyagarajan, B., Ed.; Wiley-Interscience: New York, 1971; Vol. 4, p 1. (b) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. (c) Berson, J. A. In "Rearragements in Ground and Excited States", de Mayo, P., Ed.; Academic Press: New York, 1980, p 311.

(2) Baseman, R.; Pratt, D. W.; Chow, M.; Dowd, P. *J. Am. Chem. Soc.* **1976**, *98*, 5726.

(3) Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. A. Chem. Soc.* **1976**, *98*, 5725.

(4) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.

(5) Turro, N. J.; Mirbach, M.; Harrit, N.; Berson, J. A.; Platz, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 7653.

(6) (a) Rule, M.; Mondo, J.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2209. (b) Rule, M.; Berson, J. A. *Ibid.* **1979**, *101*, 7091.

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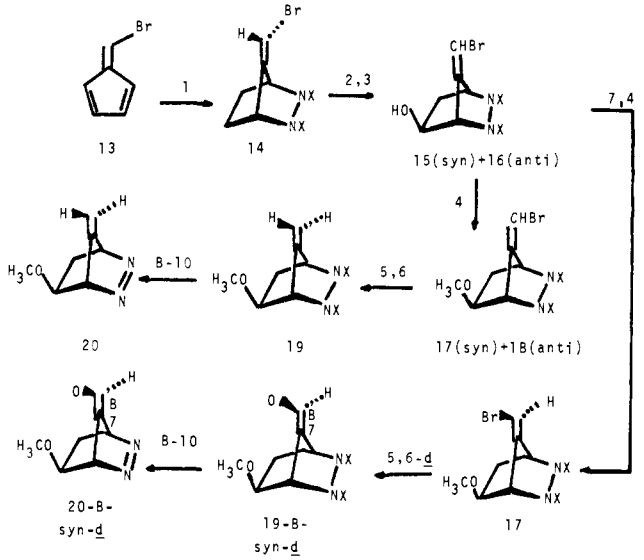
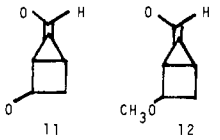
Scheme III[a] (X = CO_2CH_3)



[a] Methods: (1) $MeO_2CN{=}NCO_2CH_3$; (2) BH_3; (3) H_2O_2, NaOH; (4) NaH, CH_3I; (5) *t*-BuLi; (6) EtOH; (6-*d*) EtOD; (7) separation of crystalline isomer; (8) hot aqueous KOH; (9) H_3O^+; (10) O_2.

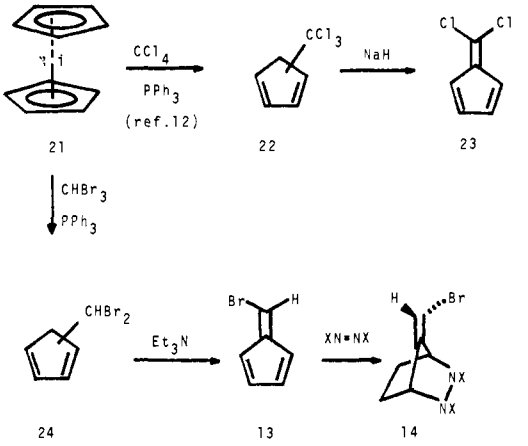
observed trimethylenemethanes, it remains to be demonstrated that the characteristic methylenecyclopropane rearrangements of Scheme I, the interception of a singlet trimethylenemethane by an olefinic trapping agent, and the spin inversion leading to a triplet trimethylenemethane *all can occur in one reactant*. These requirements are satisfied in the 5-alkylidenebicyclo[2.1.0]pentane series, as is described in the present paper for the stereomutations and in the accompanying[7] paper for the skeletal rearrangements.

For observation of stereomutations analogous to **4** → **6** in a 5-alkylidenebicyclo[2.1.0]pentane, it is necessary to incorporate two stereochemical labels, one to detect the bridgehead double epimerization and the other to detect torsion around the exocyclic double bond. The ideal substituents would be deuterium, as in **11**. However, anticipated difficulties in the synthesis of **11** have persuaded us to accept a compromise structure **12**, in which one of the deuteriums is replaced by methoxyl. We do not claim that the methoxyl group is without influence on the properties of the bicyclic compound or its related biradicals, but the results nevertheless are fully applicable to the problems being addressed here.



Syntheses of 2,3-Diaza-5-*exo*-methoxy-7-methylenenorborn-2-ene (20) and Its Stereospecifically Deuterated Analogue, 20-*8-syn-d* (Scheme III). The Experimental Section gives the details of the syntheses of the two diazenes used in this work. The unlabeled material **20** can be prepared from the syn–anti mixture of alcohols **15** + **16** without separation of the isomers. Fortunately for the synthesis of the stereospecifically labeled analogue, one of the two isomeric alcohols can be obtained in pure form by crystallization. Although the assignment as syn or anti is not critical for the present purpose, a tentative identification of the crystalline isomer as the syn compound **15** can be made by nuclear magnetic resonance (NMR) spectroscopy (see Experimental Section). This is confirmed by a single-crystal X-ray structure determination.[8] Application of the appropriate synthetic methods (see Scheme III) to **15** leads ultimately to diazene **20**-*8-syn-d*.

Scheme IV (X = CO_2CH_3)

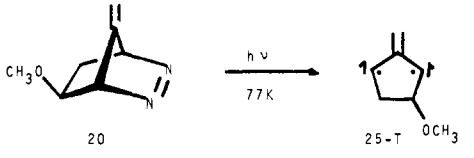


An Improved Synthesis of 6-Bromofulvene (13). In practice, the synthesis of Scheme III requires a reliable source of 6-bromofulvene (**13**). Our preliminary studies[9] used **13** prepared from cyclopentadiene, bromoform, and potassium *tert*-butoxide, in analogy to the preparation[11] of 6-chlorofulvene by a similar recipe (in which chloroform replaced bromoform). This reaction gave low yields and was difficult to carry out on a scale large enough to provide more than 1–2 g of the Diels–Alder adduct **14**.

A more efficient synthesis of **13** is inspired by the report of Moberg and Nilsson[12] that reaction of bis(cyclopentadienyl)nickel (nickelocene) with carbon tetrachloride and triphenylphosphine gave a good yield of (trichloromethyl)cyclopentadiene **22** as a mixture of double bond position isomers. The latter material was readily converted by sodium hydride to 6,6-dichlorofulvene (**23**) (Scheme IV).

Adaptation of this idea to the case of bromoform now gives a mixture of (dibromomethyl)cyclopentadienes, **24**, which can be readily dehydrobrominated to 6-bromofulvene (**13**). Immediate reaction of the product with dimethyl azodicarboxylate permits the routine preparation of 13 g of Diels–Alder adduct **14** without isolation of the intermediates. The overall yield of **14** from nickelocene **21** is 25%.

Electron Paramagnetic Resonance (EPR) Spectroscopy of the Triplet Trimethylenemethane, 4-Methoxy-2-methylenecyclopentane-1,3-diyl (25-T). Irradiation (Hg medium pressure lamp) of a sample of the diazene **20** in a 2-methyltetrahydrofuran matrix at 77 K in the microwave cavity of an EPR spectrometer leads to a strong signal characteristic of a randomly oriented triplet species. The zerofield splitting parameters (cm^{-1}), determined by procedures described elsewhere,[3] were $|D|/hc$ = 0.0269 and $|E|/hc$ = 0.0057, which closely match those of the parent 2-methylenecyclopentane-1,3-diyl (**10**, R = H). The triplet species from **20** is assigned structure **25**-T. Although a Curie plot of the EPR signal intensity vs. the inverse of absolute temperature is not yet available, analogy to several other 2-alkylidenecyclopentane-1,3-diyls[3] suggests that the triplet is the ground state of the 4-methoxy-2-methylenecyclopentane-1,3-diyl system.



Capture of Singlet and Triplet Trimethylenemethanes 25 by Cycloaddition Reactions with Cyclopentadiene. It is potentially valuable to know whether the configurational specificity in the

(7) (a) Salinaro, R. F.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2228. (b) Mazur, M. R.; Berson, J. A. *Ibid.* **1981**, *103*, 684. (c) Mazur, M. R.; Berson, J. A. *Ibid.* **1982**, *104*, 2217.

(8) Golembeski, N.; Adams, R.; Lazzara, M. G. *Cryst. Struct. Commun.*, in press.

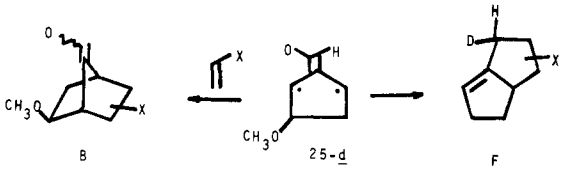
(9) Harrison, J. J. Ph.D. Thesis, Yale University, 1976; see also ref 10.

(10) Washburn, W. N.; Zahler, R.; Chen, I. *J. Am. Chem. Soc.* **1978**, *100*, 5863.

(11) D'Amore, M. B.; Bergman, R. G. *J. Chem. Soc. D* **1971**, 461.

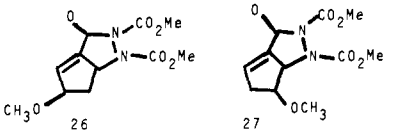
(12) Moberg, C.; Nilsson, N. *J. Organomet. Chem.* **1973**, *49*, 243.

doubly labeled diazene **20**-*8-syn-d* survives in the cycloadducts of the corresponding trimethylenemethane **25**. In particular, it would be useful to know the extent to which the deuterium on the exocyclic double bond loses configuration in the product. The fate of this label may be followed much more easily in a bridged cycloadduct (**B**) than in a fused one (F), because the NMR chemical shifts of the exocyclic protons are highly characteristic, whereas those of the saturated alicyclic protons usually are not. Unfortunately, the adducts of singlet 2-alkylidenecyclopentane-1,3-diyls with monoolefins are largely (>98%) of the fused type.[4]



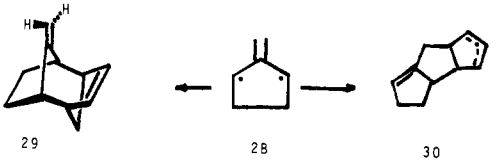
B 25-d F

We have examined the cycloadducts **26** and **27** of the quasiolefin dimethyl azodicarboxylate, in which the NMR resonances of interest are shifted downfield by the nearby nitrogen, and have been able to locate the label by ^2H NMR spectroscopy.[13] However, other serious experimental and interpretative difficulties remain in that system.[13]



26 27

A suitable alternative is suggested by the observation[14] that cyclopentadiene reacts with the unsubstituted 2-alkylidenecyclopentane-1,3-diyl singlet **28** to give about 25–30% bridged 1,4-cycloadduct **29** in addition to 70–75% of the fused 1,2 product **30**. We find that the methoxy-substituted diyl **25** also gives substantial quantities of bridged 1,4 adducts.

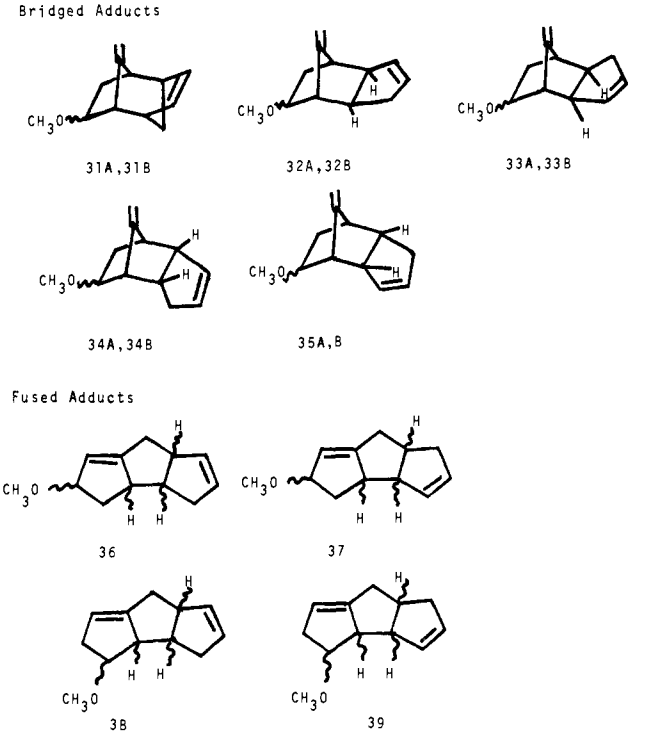


29 28 30

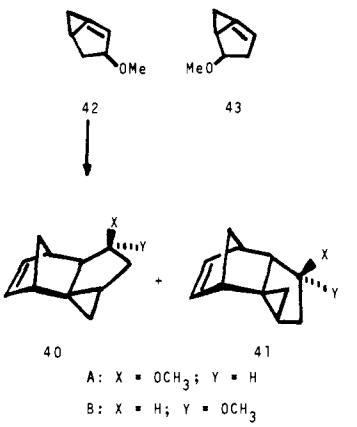
Because of the presence of the methoxy group, the number of possible cycloadducts from diyl **25** is much greater than that from the unsubstituted diyl **28**. As expected, photolysis of the methoxy-substituted diazene in acetonitrile solution containing excess cyclopentadiene gives a complex mixture of products. Mass spectroscopy, gas chromatography, and NMR spectroscopy, may be used in combination to determine the structures of the adducts. The assignments are greatly facilitated by comparisons of NMR chemical shifts with those of known[14] models lacking the methoxy group. Details of these procedures are given elsewhere.[15]

Eight of the adducts contain fused or bridged structures (**31A**, **31B**, **32A** or **33A**, **32B** or **33B**, and **36–39**) typical of TMM products and similar to those observed[14] in the unsubstituted series from diyl **28**. In addition, it is possible to identify four other 1:1 adducts (totaling 7% of the cycloadduct mixture) which seem to contain cyclopropane rings, as judged by ^1H NMR resonances at high fields (δ 0.2–1.0). Analogous cycloadducts have not been observed in previous reactions of 2-alkylidenecyclopentane-1,3-diyls, despite deliberate searches.[4,14] We suggest that these are products **40A**, **40B**, **41A**, and **41B** derived by Diels–Alder addition of cyclopentadiene to the strained double bond of the two methoxybicyclo[3.1.0]hex-1-enes, **42** and **43**. An analogous Diels–Alder adduct has been observed[16] from 1,3-diphenylisobenzofuran and a bicyclo[3.1.0]hex-1-ene generated in a different way. For reasons given below, we believe the bicyclo[3.1.0]hexanes **42** and **43** are formed from 2-methoxy-5-methylenebicyclo[2.1.0]pentane by the reverse of a thermal rearrangement exemplified in an accompanying paper.[7]

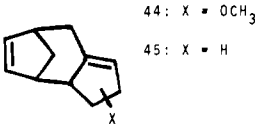
Scheme V. Cycloadducts of Diyl 28 and Cyclopentadiene[a]



[a] In structures 31–35, the A and B isomers have *exo*- and *endo*-methoxy configurations, respectively.



Aside from the presence of these minor adducts, the product mixture from the methoxy diyl **25** is quite similar to that observed[14] from the unsubstituted diyl **28**. It is especially noteworthy that the fused adducts mainly result from 1,2 addition to the diene, giving **36–39**. The alternative fused 1,4 addition would have given products of type **44**, but these are not found here, and their analogues of type **45** were shown to be absent in the products from unsubstituted diyl and cyclopentadiene.



(13) Harrison, J. J. Ph.D. Thesis, Yale University, 1976.
(14) (a) Siemionko, R.; Shaw, A.; O'Connell, G.; Little, R. D.; Carpenter, B. K.; Shen, L.; Berson, J. A. *Tetrahedron Lett.* **1978**, 3529. (b) Siemionko, R.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3870.
(15) (a) Lazzara, M. G. Ph.D. Thesis, Yale University, 1980. (b) Supplementary material available for this paper.
(16) (a) Rule, M.; Berson, J. A. *Tetrahedron Lett.* **1978**, 3191. (b) Rule, M.; Salinaro, R. F.; Pratt, D. R.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2223.

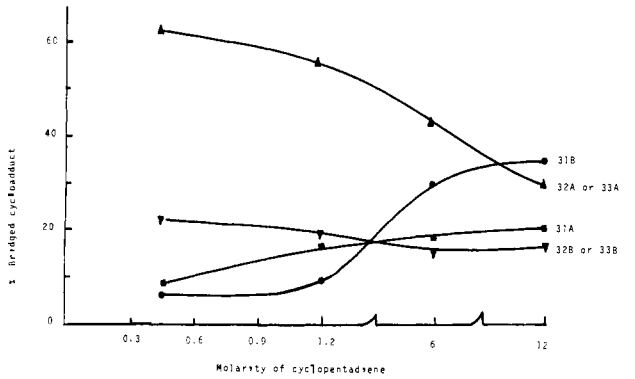
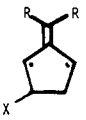


Figure 1. Concentration dependence of the relative yield of bridged cycloadducts in the photolysis of diazene **20** in excess cyclopentadiene (CH_3CN solution). The yield of bridged adducts (Scheme V) is scaled to 100%.

By analogy to the behavior of the unsubstituted (**28**)[14] and dimethyl-substituted (**51**)[4,17] diyls, the methoxy-substituted diyl **25** might be expected to show changes in the composition of the



51: R = CH_3, X = H

28: R = X = H

25: R = H, X = OCH_3

adduct mixture as the initial concentration of the trapping olefin is changed. Although the olefin always is in large excess, its ability to intercept the first-formed singlet intermediate depends on the absolute value of its concentration. If the singlet and triplet diyls give different patterns of products, a shift in the proportions of singlet-derived and triplet-derived material caused by a change in olefin concentration will lead to a change in cycloadduct composition.

With decreasing initial cyclopentadiene concentration, the unsubstituted diyl, **28**, showed an increase in the amount of bridged-1,2 adducts (**32–35**, H instead of OCH_3, Scheme V) and a decrease in the amount of bridged-1,4 adduct (**31**, H instead of OCH_3).[14] This suggested that the bridged-1,2 adducts were triplet derived and the bridged-1,4 adduct (stereospecifically syn) was singlet derived. The regio- and stereospecificity were interpreted in terms of orbital-symmetry control. The proportions of the fused-1,2-adducts (**36–39**, H instead of OCH_3) also changed with concentration.

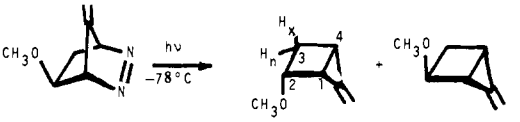
Very similar behavior is observed in the reactions of the methoxy-substituted diyl **25**. The composition of the fused adduct mixture **36–39** changes with concentration, but the most dramatic effect is observed in the bridged series (Figure 1). The two syn bridged-1,4 adducts **31A** and **31B** both increase with increasing cyclopentadiene concentration. Although we cannot guarantee that 12 M olefin suffices to produce "pure singlet" cycloadducts, the trends of the dilution effects qualitatively parallel those in the unsubstituted case.[14] In particular, they show that bridged-1,4 adducts (**31A** and **31B**) are favored products from the first-formed intermediate, which in all probability is the singlet biradical **25**. At low concentrations of cyclopentadiene, this species can undergo intersystem crossing to the corresponding triplet, which the EPR study suggests to be the more stable biradical.

The 2-Methoxy-5-methylenebicyclo[2.1.0]pentanes. Irradiation at 350 nm of a degassed solution of the diazene **20** in $CDCl_3$/$CFCl_3$ at −78 °C in an NMR sample tube produces a 3:1 mixture

Table I. Proton NMR Spectra of the 2-Methoxy-5-methylenebicyclo[2.1.0]pentanes in $CDCl_3$/$CFCl_3$ at −78 °C

assignment	chemical shift, δ major isomer (46)	chemical shift, δ minor isomer (47)
CH_2=	5.25	5.25
C-2-H	4.13	3.61
CH_3O-	3.24	3.37
endo-C-3-H	2.55	2.09
C-1-H	2.49	2.43 (or 2.34)
C-4-H	2.14	2.34 (or 2.43)
exo-C-3-H	1.65	2.11

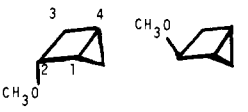
of the stereoisomeric 2-methoxy-5-methylenebicyclo[2.1.0]pentanes, **46** and **47**. These compounds are detected by rapid transfer of the tube into the precooled probe of the 270-MHz spectrometer. Table I shows the ^1H NMR resonances of the two isomers. The assignments of the proton positions are supported by spin-decoupling experiments described in the Experimental Section.



20 46 47

Specific identification of the major and minor isomers is not of particular importance to the present study, since our conclusions remain unaffected even if the stereochemical structures are reversed. Nevertheless, the NMR data favor a tentative assignment of structures **46** and **47** respectively to the major and minor isomers. The lanthanide shift reagent Eu(fod)$_3$ (tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium) shifts the olefinic methylene resonances of the major isomer (**46**) downfield more effectively than those of the minor one (**47**), as would be expected if complexation occurs at the methoxy group.

Additional evidence for the stereochemical assignments comes from comparison of the chemical shift differences of Table I with those observed by Allred and Smith[18] for the analogous 2-methoxybicyclo[2.1.0]pentanes **48** and **49**. Thus the resonance of the C-2 proton of **49** is shifted upfield by 0.5 ppm relative to that of **48**, presumably because of the shielding effect of the cyclopropane ring.[18] Similarly, the methoxy proton resonances of **48** occur 0.15



48 49

ppm upfield from those of **49**.[18] The corresponding isomeric shift differences for the C-2 and CH_3O protons in Table I are comparable in direction and magnitude.

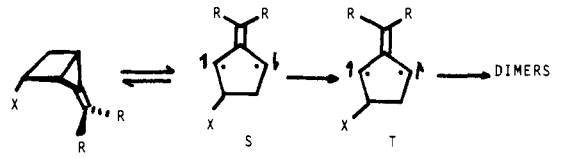
Thermal Reactions of the 2-Methoxy-5-methylenebicyclo-[2.1.0]pentanes. The title compounds undergo three new thermally induced transformations: (i) conversion of the minor isomer **47** to the major one **46** by bridgehead double inversion; (ii) formation of dimers of the trimethylenemethane biradical **25**; (iii) stereomutation by 180° torsion about the exocyclic double bond, observed in the monodeuteriated series.

The **47** → **46** reaction can be observed by raising the temperature of the NMR probe to −60 °C and monitoring the absorbances of the exocyclic methylene protons relative to the $CHCl_3$ contaminant as internal standard. The resonance of the minor isomer disappears with a half-life of about 30 min. No new absorptions appear, but the intensity of the exocyclic methylene resonance of the major isomer increases. Recooling the probe to −78 °C does not restore the signals of the minor isomer **47**. This indicates that the spectrum observed at −60 °C is not produced

(17) (a) Berson, J. A.; Duncan, C. D.; Corwin, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 6175. (b) Berson, J. A.; Corwin, L. R.; Davis, J. H. *Ibid.* **1974**, *96*, 6177. (c) Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *Ibid.* **1980**, *102*, 276. (d) Duncan, C. D.; Corwin, L. R.; Davis, J. H.; Berson, J. A. *Ibid.* **1980**, *102*, 2350.

(18) (a) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1967**, *89*, 7133. (b) Allred, E. L.; Smith, R. L. *Ibid.* **1969**, *91*, 6766.

Scheme VI



46: X=OCH_3; R=H
50: X=H; R=CH_3
52: X=R=H

25: X=OCH_3; R=H
51: X=H; R=CH_3
53: X=R=H

by a coalescence of the absorptions of the two isomers but rather records an irreversible change **47** → **46**.

The kinetics of this reaction, measured at three temperatures spanning about 13 °C, are first order, although the number and range of temperatures do not suffice for an accurate estimate of Arrhenius parameters ($E_a \sim 13 \pm 2.5$ kcal/mol, log (A in s) = 10 ± 2.4). Since the C-1–C-4 bond must be at least 25 kcal/mol weaker than any other C–C bond of **47**, we assume that the observed stereomutation involves that bond. On the further assumption that $\Delta S^{\ddagger} \sim 0$ eu, the observed average value $\Delta G^{\ddagger} = 15.7$ kcal/mol may be taken as an upper limit for the energy required to dissociate the C-1–C-4 bond and produce the singlet biradical.

The thermal reaction **47** → **46** observed with the mixture of stereoisomers at −60 °C amounts to a selective pyrolysis of the minor isomer. At higher temperature, with a practical threshold near +5 °C, the remaining pure major isomer **46** undergoes further reaction which converts it to the dimers of the trimethylenemethane biradical **25**. The products presumably have structures analogous to those observed[4,6,19] in the dimerization of 2-isopropylidenecyclopentane-1,3-diyl (**51**), although the presence of the methoxyl function in **25** greatly increases the number of possible isomeric dimers.

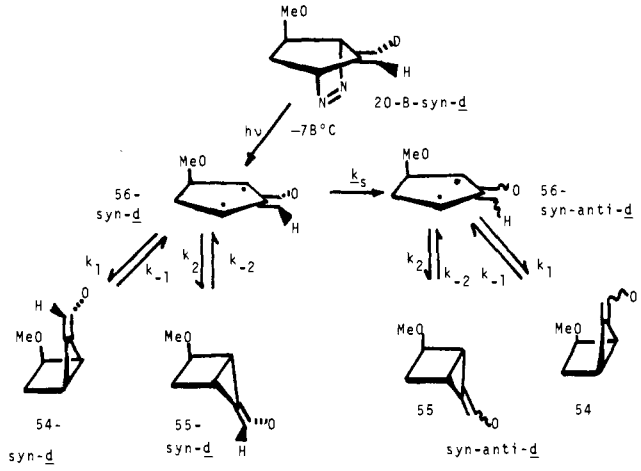
The kinetics of thermolysis of **46** are strictly first order, despite the fact that the sole products are composed of two units of starting material. This behavior parallels that of 2-isopropylidenecyclopentane-1,3-diyl (**51**) generated from 5-isopropylidenebicyclo[2.1.0]pentane (**50**)[6,7b,c] and may be interpreted in the same way, namely as the consequence of a unimolecular rate-determining step, the formation of the triplet biradical (T, Scheme VI).

Substitution has a profound effect on the thermal stability of 5-alkylidenebicyclo[2.1.0]pentanes. The approximate threshold temperatures for dimerization of the compounds **46**, **50**, and **52** at a convenient rate are 5, −40, and −60 °C, respectively. Although a study of the parent compound, **52**, is not yet complete, Arrhenius parameters for **50**, E_a = 13.6 kcal/mol, log (A in s) = 9.5, have been reported,[6,7b] and the present work provides the values E_a = 16.9 ± 1 kcal/mol, log (A in s) = 9.8 ± 1 for **46**. Evidently, the major reason for the greater thermal stability of the methoxy compound **46** lies in the higher activation energy. The chemical interpretation of this difference is still obscure, primarily because it is not certain which step of the mechanism of Scheme VI is most affected by the change of substituents from **50** to **46**.

The low Arrhenius pre-exponential term observed for **46** matches that observed[6,7b,c] for **50** and invites a similar interpretation as a manifestation of spin-forbidden character in the rate-determining step.

Synthesis of Stereospecifically Methylene-Deuterated 2-Methoxy-5-methylenebicyclo[2.1.0]pentane. Photolyses of the stereospecifically labeled diazene **20**-*8-syn-d* (~90% isotopically enriched, see Scheme III) in $CDCl_3/CFCl_3$ or toluene-d_8 solutions at −78 °C give mixtures of the two isomeric 2-methoxy-5-methylenebicyclo[2.1.0]pentanes, **54** and **55**, in which the deuterium on the exocyclic methylene group is partially but not completely scrambled. The ratio (R) of the intensities of the two methylene ^{1}H NMR absorptions is 2.0 (anti/syn) for both the *endo*- and *exo*-methoxy isomers, **54** and **55**. This equivalence is simply (if not uniquely) interpreted in terms of a mechanistic branching point at a common intermediate, which can be partitioned competitively among three pathways: stereochemical scrambling by torsion about the exocyclic partial double bond and ring closures to **54** and **55** (Scheme VII). Although the singlet trimethylenemethane **56**-*syn-d* is the most economical formulation of the intermediate, other evidence in this and accompanying papers[6,7] suggests that beyond mere convenience, the hypothesis has advantages as a plausible description of the actual course of the photodeazetation.

Scheme VII



The ratio of 2.0 for the anti/syn exocyclic methylene proton absorptions of the photochemically generated bicyclopentanes corresponds to a product ratio of ~34% stereospecifically labeled *syn-d* and ~56% stereorandomized *syn-anti-d* in both **54** and **55** (Scheme VII). The remaining 10% of the product is from the undeuterated portion of the starting material.

With the assumptions that the concentrations of the biradicals **56**-*syn-d* and **56**-*syn-anti-d* are given by the steady-state approximation and that the reaction temperature is low enough to keep the ring-opening rate constants k_{-1} and k_{-2} negligibly small, the ratio of scrambled to stereospecifically labeled products **54** or **55** may be expressed as

$$(syn\text{-}anti\text{-}d)/(syn\text{-}d) = k_s/(k_1 + k_2) \qquad (1)$$

Substitution of the experimental value 56/34 for the left-hand side of eq 1 gives us the information that the rate constant k_s for scrambling the stereochemistry of the biradical **56**-*syn-d* by exocyclic torsion is about 1.6 times the sum of the ring-closure rate constants at −78 °C. Moreover, the product ratio **54**/**55**, ~3, may be interpreted on the basis of Scheme VII as a direct measure of the competition between the two modes of ring closure.

Torsion about the Exocyclic Double Bond of 2-Methoxy-5-methylenebicyclo[2.1.0]pentane. As is expected from the observations in the unlabeled series, the labeled minor isomer **55**-*syn-d* rearranges to the major one with a half-life of about 30 min at −60 °C. Since the rearrangement is unidirectional as judged by NMR (~5% detection limit), the equilibrium constant for the reaction **55** ⇌ **54** is ≥ 19, which corresponds to a free-energy difference that favors the endo isomer **54** by at least 1250 cal/mol. It seems unlikely that the $\Delta G°$ value is much larger than this, since Allred and Smith[18] find that the equilibrium favoring the endo isomer **48** of the structurally similar 2-methoxybicyclo[2.1.0]pentane pair (**48** and **49**) corresponds to $\Delta G° \sim 1700$ cal/mol.

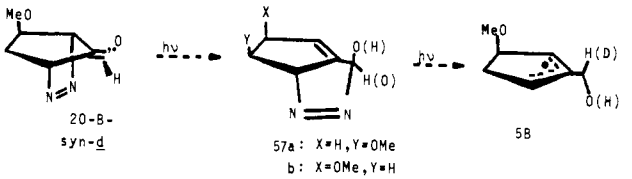
The most plausible pathway for the double epimerization **55** → **54** involves the singlet trimethylenemethane biradical **56** as the key intermediate (Scheme VII). Since this same species is held to be responsible for the partial scrambling of the exocyclic deuterium label observed during the photolysis (at an even lower temperature) of the diazene **20**-*8-syn-d*, it follows that further scrambling of both **55** and **54** should accompany the thermal double epimerization **55** → **54**.

(19) Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. *J. Am. Chem. Soc.* **1971**, *93*, 1541.

The most sensitive portion of the NMR spectrum in which to attempt to observe the predicted scrambling is in the exocyclic methylene resonances of the minor isomer. However, scrutiny of the ratio of anti/syn proton resonances for either isomer during the **55** → **54** reaction fails to reveal any diminution from the value of 2.0 observed in the original products of photolysis of diazene **20**-*8-syn-d*.

At first glance, this seems to contradict the mechanism proposed for either the photochemical or the thermal portion of Scheme VII, since the alleged common intermediate does not seem to behave consistently. Although the photochemical deazetation of the diazene **20** is not a major concern of the present work, the understanding of analogous processes does play an important role elsewhere.[6,7] Accordingly, we consider two possible alternative photochemical mechanisms.

The first involves two competing pathways from the excited diazene. One generates **54**–**55**-*syn-d* stereospecifically, and the other causes rearrangement of the bridged diazene **20** to either or both of the fused diazenes **57a** and **57b**. Regardless of the direction in which the exocyclic methylene group twists in the formation of fused diazene, the stereochemical integrity of the label would be compromised, since deazetation now could give a bisected trimethylenemethane **58** with an indeterminate stereorelationship between OMe and D.



Although this hypothetical pathway requires two photons and hence, in principle, is subject to direct experimental test, we have not done so. At present, the only argument against such a possibility is the analogy to the photodeazetation of the bridged diazene **8** (R = Me) which has been shown[20] specifically not to be accompanied by rearrangement to a fused isomer.

A second alternative hypothesis would involve formation of a twisted singlet trimethylenemethane from the photochemical reaction, rather than the planar species shown in Scheme VII. We have no direct argument against this possibility, which in principle could be tested by trapping experiments similar to those used[7] in the case of diazene **8** (R = Me), provided that the twisted trimethylenemethane is a metastable intermediate. Thus, photolysis of **20**-*8-syn-d* in the presence of an olefin at low temperature should permit interception of the twisted species as a cycloadduct in which the MeO vs. D stereochemistry would be retained if the planar diyl were involved but would be partially or fully scrambled if the twisted species were the intermediate. Although future observations may necessitate the postulation of geometrically distinct structures for the singlet species derived by photodeazetation of the diazene **20** and by thermolysis of the bicyclopentanes **54** and **55**, the evidence so far does not make a compelling case for such a hypothesis.

The search for scrambling during the double epimerization reaction is hampered by the low stereospecificity of the labeling in the samples of **55**-*syn-d* available from the present synthesis. Moreover, after pyrolysis to near completion of the **55** → **54** rearrangement, when any scrambling in **55** should be most evident, the NMR absorptions of the exocyclic methylene protons of **55** are partially overlapped by those of **54**. This makes integration of the peaks difficult and leaves open the possibility that the apparent absence of exocyclic torsion during the thermal double epimerization **55** → **54** may be illusory.

Exocyclic torsion does become apparent when the temperature of the sample of the remaining major isomer **54**-*syn-d* is raised to −40 °C. The ratio of intensities of the anti/syn exocyclic methylene protons declines from 2.0 to the equilibrium value of 1.0 with a half-life of about 15 min ($k \sim 7.7 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger}$ = 17 000 cal/mol) in either $CDCl_3/CFCl_3$/Eu(fod)$_3$ or toluene-d_8 solutions.

Finally, like its counterpart in the undeuterated series, **54**-*d* suffers ring opening and dimerization at temperatures above 5 °C.

Stereorandomization during Cycloadduct Formation. Photolysis of the stereospecifically labeled diazene **20**-*8-syn-d* in neat cyclopentadiene solution at 0 °C gives the same mixture of adducts observed in the undeuterated series. Isolation of the bridged compounds (**31**–**35**, Scheme V) by GC and individual analyses by NMR show that the exocyclic deuterium configuration is completely scrambled in each case. Control experiments show that the starting diazene **20**-*syn-d* can be recovered after partial photolysis with completely preserved stereospecificity of the label and that the total deuterium content of the cycloadducts is the same as that of the diazene. The latter observation rules out adventitious acid-catalyzed stereoequilibration.

A full interpretation of the scrambling in the cycloadditions cannot be given at the moment, because under these conditions the cycloadducts can be formed in two ways: (1) direct interception of the photochemically generated singlet TMM intermediate(s) before ring closure, or (2) reaction with the bicyclopentanes **54** and **55**, probably via initial thermal reversion of the latter to a singlet biradical.[7b,c] If the second pathway operates exclusively, the formation of extensively or completely scrambled cycloadducts would not be surprising, since the exocyclic torsion (e.g., **54**-*syn-d* → **54**-*syn-anti-d*) is fast at 0 °C. If the first pathway operates, it becomes necessary to postulate that only the stereorandomized diyls are intercepted. One could imagine reasons for this, for example, if competitive intramolecular ring closure were fast from the stereospecifically labeled planar diyl (**56**-*syn-d*, Scheme VII) but slow from the effectively stereorandomized, bisected diyl. For the present, further speculation seems unwarranted.

The same series of cycloadducts is obtained when excess cyclopentadiene is added to a $CDCl_3/CFCl_3$ solution of the mixed bicyclopentanes **54** and **55** and allowed to warm to 0 °C. Moreover, when the same reaction is carried out with the stereospecifically labeled compounds **54**-*syn-d* and **55**-*syn-d*, completely scrambled cycloadducts again are formed.

The presence in the cycloadduct mixtures of small amounts of the Diels–Alder adducts **40** and **41**, derived from the bicyclo[3.1.0]hex-1-enes **42** and **43**, is noteworthy. The latter compounds do not seem to be formed during the photolysis of the diazene **20** at −78 °C. Scrutiny of the NMR spectrum of the mixture of bicyclopentanes **54** and **55** resulting from that photolysis fails to disclose the presence of the $\pi + \pi$ cyclodimers[6,7a,16,21] (e.g., **59**) that **42** and **43** should have afforded. Even during the studies of stereomutations **55** → **54** at −60 °C and **54**-*syn-d* → **54**-*syn-anti-d* at −40 °C, products such as **59** are not observed. We assume that the bicyclo[3.1.0]hex-1-enes **42** and **43** are formed from the 5-methylenebicyclo[2.1.0]pentanes **54** and **55** by a rearrangement which has a practical threshold temperature above −40 °C. This transformation is an example of the reverse of the 5-alkylidenebicyclo[2.1.0]pentane → bicyclo[3.1.0]hex-1-ene rearrangement described elsewhere.[7a,22] (We think it is unlikely that **40** and **41** are formed by a concerted $[\pi + \pi + \pi + \sigma]$ cycloaddition directly between cyclopentadiene and **54** or **55**.) Of course, it does not follow that the equilibrium position in the methylenebicyclo[2.1.0]pentane (**54**,**55**)–bicyclo[3.1.0]hex-1-ene

(20) (a) Cichra, D.; Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 8507. (b) Cichra, D. A.; Duncan, C. D.; Berson, J. A. *Ibid.* **1980**, *102*, 6527.

(21) Köbrich, G.; Heinemann, H. *J. Chem. Soc., Chem. Commun.* **1969**, 493.

(22) Salinaro, R. F.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7094.

(23) (a) Ullman, E. F. *J. Am. Chem. Soc.* **1959**, *81*, 5386. (b) Ullman, E. F. *Ibid.* **1960**, *82*, 505. (c) Ullman, E. F.; Fanshawe, W. J. *J. Am. Chem. Soc.* **1961**, *83*, 2379.

(24) (a) Doering, W. von E.; Roth, H. D. *Tetrahedron* **1970**, *26*, 2825. (b) Doering, W. von E.; Birladeanu, L. *Ibid.* **1973**, *29*, 499.

(25) Roth, W. R.; Wegener, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 758.

(26) Gajewski, J. J.; Chou, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 5696.

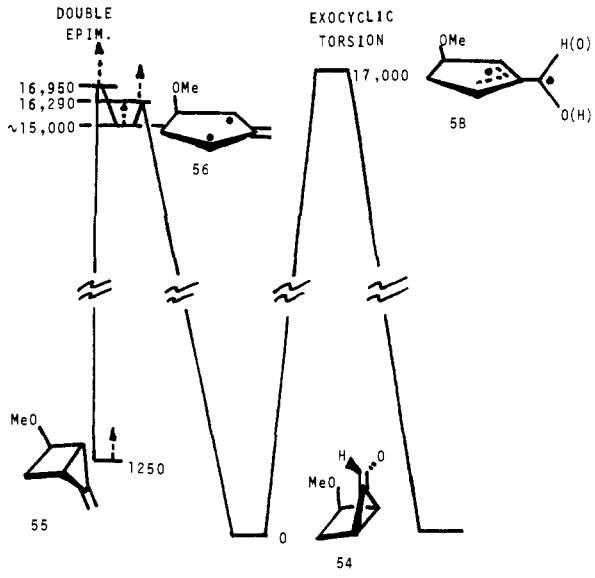
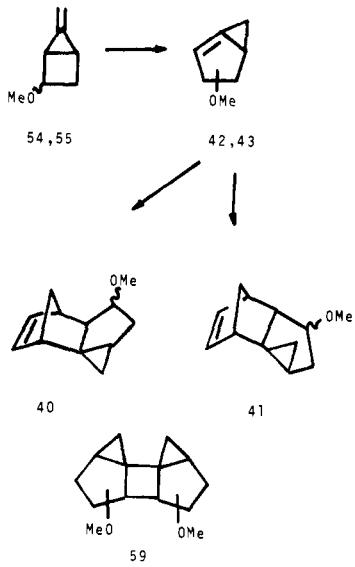


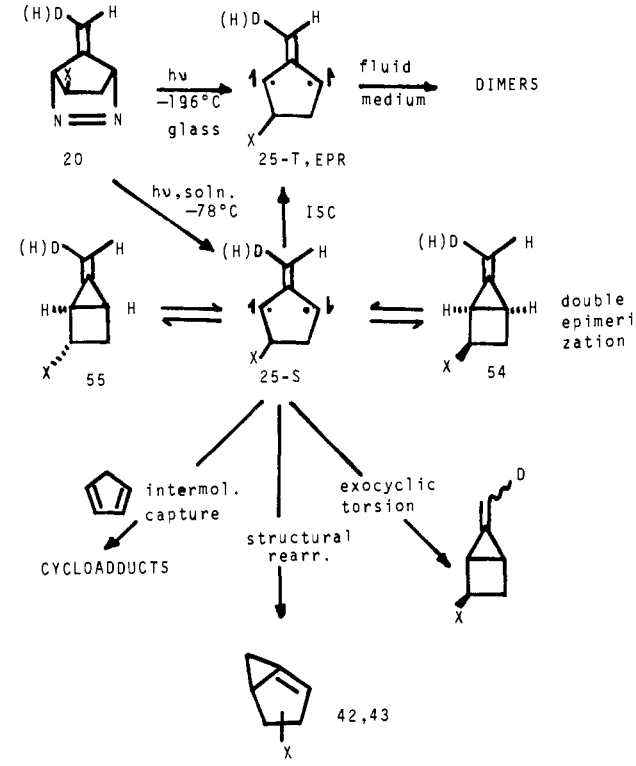
Figure 2. Free-energy surface for the stereomutations of the 2-methoxy-5-methylenebicyclo[2.1.0]pentanes. The numbers alongside the horizontal lines represent values of $\Delta G°$ relative to that for **54**, which is arbitrarily assigned as the reference state. Energy levels denoted with an upward-pointing arrow are known only as lower limits.

(**42**,**43**) interconversion favors the latter system or even that the proportion of **42**,**43** in equilibrium with **54**,**55** is the same as the 7% of cycloadducts **40**,**41** observed.



The Energy Surface for the 2-Methoxy-5-methylenebicyclo[2.1.0]pentane Stereomutations. The Energy Separation between the Planar and Bisected Singlet Trimethylenemethanes. The data given above permit the display of a relative free-energy surface (Figure 2) for the stereomutations. The ΔG values necessarily derive from experiments at more than one temperature, but if we make the reasonable assumption that the entropies of the various species do not differ greatly, the $\Delta G°$ values are comparable. From the minimum value of the equilibrium constant between the endo and exo isomers **54** and **55**, we obtain a minimum endoergicity of formation of 1250 cal/mol for the exo compound **55**. The observed $\Delta G^{\ddagger}$ for the double epimerization **55** → **54**, 15,700 cal/mol, when added to this, gives $\Delta G°$ (16 950 cal/mol) of the transition state for formation of the singlet biradical **56** from **55**. If we assume that the same biradical is the intermediate in the photodeazetation of diazene **20** (see Scheme VII), we may use the 3:1 product ratio **54**:**55** to calculate a $\Delta G°$ = 16 290 cal/mol for the transition state for ring closure of **56** to the endo isomer **54**. A $\Delta G°$ for biradical **56** itself cannot be obtained from the

Scheme VIII (X = OCH_3)



data in this paper. However, the activation energy for ring closure of 2-isopropylidenebicyclo[2.1.0]pentane is estimated[7b,c] to be about 2000 cal/mol. If we assume a similar barrier for the ring closure of the analogous biradical **56**, $\Delta G°$ for this species would be about 15 000 cal/mol.

The transition state for the exocyclic torsion in **54**, as measured by the rate of scrambling of the deuterium label, falls at 17 000 cal/mol. It is not obvious whether this transition state is achieved only after preliminary ring opening to the planar species **56** or by a direct ring opening *cum* torsion. Moreover, it is uncertain that this transition state has a strictly bisected structure, since such a species might represent a local energy minimum. Nevertheless, the exocyclic bond in the transition state cannot be other than severely twisted, and for the purpose of the present discussion, we assume that the energy of the bisected species is essentially the same as that of the transition state. On this basis, the energy of the planar diyl **56** lies no more than about 2000 cal/mol below that of the bisected one **58**. Because $\Delta G°$ for planar biradical **56** is known only as a lower limit, the possibility exists that the energy ordering shown in Figure 2 may be reversed and that the bisected diyl **58** may be more stable than the planar one **56**.

These results are at least qualitatively in agreement with the low planar-bisected rotational barriers observed[1,23-26] and calculated[27-31] for other trimethylenemethane singlet biradicals.

Experimental Connection between the Spectroscopically Observed Triplet Biradical and the Reactive Intermediates in Thermal Stereomutation and Cycloaddition. Scheme VIII summarizes the mechanistic and experimental relationships established in this study. The triplet biradical **25**-T can be generated by photolysis of the diazene **20** and observed spectroscopically by EPR. In a glassy medium at −196 °C, the EPR signal persists even after irradiation ceases, which suggests a low-lying (probably ground) triplet state. This hypothesis is confirmed by the dilution effect

(27) Yarkony, D. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1974**, *96*, 3754.
(28) (a) Davis, J. H.; Goddard, W. A., III *J. Am. Chem. Soc.* **1976**, *98*, 303. (b) Davis, J. H.; Goddard, W. A., III *Ibid.* **1977**, *99*, 4242.
(29) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1977**, *99*, 2053.
(30) Dixon, D. A.; Foster, R.; Halgren, T. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 1359.
(31) For a review, see: Borden, W. T.; Davidson, E. R. *Annu. Rev. Phys. Chem.* **1979**, *30*, 125.

on the composition of the cycloadduct product mixture when the photolysis of **20** is carried out in fluid solution in the presence of cyclopentadiene.

Photolysis of **20** in fluid medium at −78 °C gives the stereoisomeric 5-methylenebicyclo[2.1.0]pentanes **54** and **55**, which interconvert by double epimerization at the exocyclic position of **54**, syn–anti scrambling of the label occurs at −40 °C. The present work strongly suggests and accompanying work[7a] on an analogous system confirms structural rearrangement (e.g., **54,55** → **42,43**) at temperatures somewhere above −40 °C.

Finally, at temperatures above 5 °C, the bicyclic compounds **54** and **55** suffer ring opening and intersystem crossing (ISC) to the triplet **25-T**, which goes on to dimers. In this transformation, although the competition for disposal of the single **25-S** is unfavorable to ISC at temperatures higher than the rearrangement and torsion thresholds, the absolute rate of formation of the singlet diyl also is increased, and this permits dimer formation to be observed.[32]

The present and accompanying[7a,22] works demonstrate that the characteristic structural and stereochemical rearrangements of methylenecyclopropanes, which occur by way of singlet biradicals, can be observed in the same systems that permit direct spectroscopic observation of the biradical's triplet ground state.

Experimental Section

Instruments and Techniques. Routine nuclear magnetic resonance (NMR) spectra were taken on a Perkin-Elmer R-32, 90 MHz spectrometer in deuteriochloroform or carbon tetrachloride. Chemical shifts were measured relative to tetramethylsilane (Me_4Si). High-quality ^1H NMR spectra, double resonance ^1H NMR spectra, low-temperature ^1H NMR spectra, pulse-delayed ^1H NMR spectra, and kinetic data were obtained on a Bruker HX270 instrument.

Infrared (IR) spectra were recorded on either a Perkin-Elmer Model 237 or Beckman IR4250 spectrometer. EPR spectra were obtained with the Varian E-9 system.

Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6 single-focusing instrument or a Hewlett-Packard 5985A GC/MS instrument. High-resolution mass spectra were taken on an AEI-MS-902 by Dr. William Bailey of the Department of Chemistry at the University of Connecticut.

Analytical GC was performed on a Perkin-Elmer 900 gas chromatograph equipped with a flame ionization detector and utilizing nitrogen as a carrier gas. For all analytical studies a 0.125 in. packed column was used. Preparative GC was carried out on a Varian Aerograph 90-P-3 with helium as the carrier gas. All preparative GC utilized 0.250 in. packed columns. GC peak integrals were obtained by weighing the peak which was cut out from a xerographic copy of the chromatogram. Usually five such weighings were done for each peak.

GC Columns Used were the following: A, 20 ft by $^1/_8$ in. 3% OV-17 on 80–100 mesh Anakrom ABS; B, 10 ft by $^1/_4$ in. 10% OV-17 on 60–80 mesh Anakrom ABS; C, 5 ft by $^1/_8$ in. 3% γ-methyl-γ-nitropimelonitrile on 80–100 mesh Chromosorb P; and D, 5 ft by $^1/_4$ in. 5% γ-methyl-γ-nitropimelonitrile on 60–80 mesh Chromosorb P.

Melting points were taken on a Thomas Hoover Capillary melting point apparatus and are uncorrected.

Elemental analyses by combustion were performed by Dr. R. C. Rittner, Olin Chemical Co.

Reagents. Chemicals used were reagent grade or better. Solvents were purified according to procedures recommended in the literature.[33]

Standard Procedures. All reactions were performed under a positive pressure of nitrogen with glassware which was flame dried under a nitrogen flow.

Photolysis tubes were made from 4–7-mm Pyrex tubing cut into 30-cm lengths. These were rinsed with ammonium hydroxide and distilled water and air dried. The open tubes were divided in the middle with an oxygen flame and then oven dried until needed.

Stock solutions were made by weighing components to ±0.1 mg on a Mettler H20T balance into a 1-mL volumetric flask. Solvent and/or cyclopentadiene was added to the mark with a Hamilton syringe. Stock solutions and solvents were measured into sample tubes with a microsyringe, and the tubes were degassed on a vacuum line. The samples were frozen in liquid nitrogen and the stopcock was opened to the vacuum. The stopcock was then closed and the solution warmed gently to room temperature (from top to bottom to prevent tube explosion upon warming). The tube was then refrozen, reevacuated, and rewarmed. This process was carried out four times, after which the tube was sealed with an oxygen flame.

Photolyses were run in a Rayonet reactor (Southern New England Ultraviolet Co.) which contained sixteen 350-nm lamps. The sample tubes were suspended from a bored out rubber stopper into an unsilvered Dewar cylinder. The tubes were surrounded by one of four media to maintain a specific temperature: 0 °C, ice/water; −78 °C, dry ice/ethanol (95%); −80 to −120 °C, cooled nitrogen gas; −196 °C, liquid nitrogen. Photolyses were run for varying lengths of time (see specific experiment). Temperatures were monitored with a Leeds and Northrup Co. potentiometer No. 8691 with copper–constantan thermocouples.

For all kinetic experiments, NMR tubes (5 mm) replaced Pyrex tubes for the photolyses. They were degassed and sealed in the same fashion as their Pyrex counterparts.

7-Bromomethylene-*N*,*N*-dicarbomethoxy-2,3-diazabicyclo[2.2.1]hept-5-ene (14) (Scheme III). A. 6-Bromofulvene (13). A 1-L, three-neck, round-bottom flask, equipped with a mechanical stirrer, additional funnel, and nitrogen inlet, was charged with nickelocene (30 g; 0.159 mol), triphenylphosphine (41.7 g; 0.159 mol), and 400 mL of dry diethyl ether. A solution of bromoform (40.2 g; 0.159 mol), in 50 mL of ether, was added dropwise to the stirred suspension. The reaction mixture was stirred for 17 h. The insoluble materials were removed by suction filtration, and the residue was rinsed twice with 50-mL portions of ether. The filtrate was placed in a 2-L, three-neck, round-bottom flask equipped with a mechanical stirrer and a nitrogen inlet. Triethylamine (16.1 g; 0.159 mol) was added to the cooled (ice bath) filtrate and the resulting mixture was stirred for 5 min at 0 °C. The triethylamine hydrobromide which had formed was filtered off. The filtrate was placed back into the 2-L flask and to it were added 500 mL of 1 M $CuCl_2$(aq). The two-phase mixture was stirred very rapidly for 5 min, after which it was passed through Celite 545 to remove the white precipitate formed. The aqueous layer was removed and the organic layer containing 6-bromofulvene (**13**) was washed three times with 100-mL portions of water. The organic extracts were dried over Na_2SO_4.

B. Diels–Alder Adduct 14. Dimethyl azodicarboxylate (14.6 g; 0.1 mol) was added to the organic layer and the resulting mixture concentrated to a volume of 100 mL. This material was stirred under a positive pressure of nitrogen for 24 h at room temperature.

Any excess of dimethyl azodicarboxylate could be removed by the following procedure: A solution of crude **14** in 500 mL of ether was poured slowly into a 2-L Erlenmeyer flask containing a solution of saturated Na_2CO_3(aq) which was being stirred. The mixture was stirred until the bubbling ceased. The aqueous layer was removed, and the ether layer was washed several times with water in 100-mL portions and dried over Na_2SO_4. Concentration of the solvent afforded a brown oil which was subjected to column chromatography on 200 g of Florisil. Elution with benzene provided 6-bromofulvene dimer and excess bromoform. By flushing the column with benzene/ethyl acetate (8:1), fairly pure Diels–Alder adduct **14** could be obtained in yields of 20–25%. Crystallization of **14** was effected by dissolving the pale yellow oil obtained from the column chromatography in 30 mL of ether, seeding, and storing the solution at 4 °C for 24 h to give white crystals, mp 107–107.5 °C. Material of mp 110.5–112.5 °C was obtained by recrystallization from ether. NMR ($CDCl_3$) δ 3.78 (s, 6 H, CO_2CH_3), 5.20 (br s, 1 H, bridgehead), 5.45 (br s, 1 H, bridgehead), 5.73 (s, 1 H, vinyl H), 6.71 (t, 2 H, vinyl H's, J = 2 Hz). Anal. Calcd for $C_{10}H_{11}N_2O_4Br$: C, 39.62; H, 3.66; N, 9.24; Br, 26.36. Found: C, 39.82; H, 3.79; N, 9.32; Br, 26.47.

5-*exo*-Hydroxy-7-bromomethylene-*N*,*N*-dicarbomethoxy-2,3-diazabicyclo[2.2.1]heptanes 15 and 16. Diels–Alder adduct **14** (5.0 g; 16.5 mmol) was dissolved in 50 mL of dry tetrahydrofuran (THF) and added dropwise with stirring to 24.8 mL of 1 M BH_3/THF complex and 110 mL of additional THF at 0 °C over a period of 30 min. The mixture was then allowed to warm to room temperature and stir over a period of 2 h. The solution was recooled to 0 °C and water cooled to 4 °C was added carefully until all the excess borane was discharged. A solution of 7 mL of 30% hydrogen peroxide and 15 mL of 1 M sodium hydroxide, which had been thoroughly mixed and precooled to 4 °C, was added dropwise over a period of 10 min with stirring. The resulting mixture was allowed to warm to room temperature and with stirring over a 2-h period. To the mixture was added 20 mL of ether. The solution was washed three times with brine and dried over Na_2SO_4. A yellow oil resulted after the solvent was removed in vacuo. The crude reaction mixture was dissolved in acetone and 1.47 g (28%) of the syn isomer **15** crystallized out: mp 187–190 °C; NMR ($CDCl_3$) δ 6.40 (s, 1 H, vinyl H), 5.00 (m, 1 H, bridgehead), 4.72 (m, 1 H, bridgehead), 4.50 (s, 1 H, OH), 4.20 (m, 1 H, CHOR), 3.80 (s, 6 H, CO_2CH_3), 2.24 (m, 1 H, endo H), 1.68 (m,

(32) For a discussion, see ref 6.

(33) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", Pergamon: Oxford, England, 1966.

(34) Gallinella, E.; Mirone, P. *J. Labeled Compd.* **1967**, *7*, 183.

1 H, exo H). Anal. Calcd for $C_{10}H_{13}N_2O_5Br$: C, 37.40; H, 4.08; N, 8.72. Found: C, 37.20; H, 4.15; N, 8.56.

The mother liquor was then purified by column chromatography on 250 g of Florisil. Elution with benzene and then with benzene/ethyl acetate (8:1) yielded unreacted Diels–Alder adduct and fragmented material. Elution with benzene/ethyl acetate (1:1) yielded a colorless oil. The oil was dissolved in acetone and an additional 0.42 g of **15** (8%) precipitated out. The mother liquor, an oil (1.94 g/37%), was a mixture of the alcohols enriched in the anti isomer **16** in approximately a 5:1 ratio. The NMR of **16** is as follows: ($CDCl_3$) δ 6.32 (s, 1 H, vinyl H), 5.00 (m, 1 H, bridgehead), 4.80 (m, 1 H, bridgehead), 4.50 (s, 1 H, OH), 4.20 (m, 1 H, CHOR), 3.80 (s, 6 H, CO_2CH_3), 2.24 (m, 1 H, endo H), 1.68 (m, 1 H, exo H).

5-exo-Methoxy-7-bromomethylene-*N*,*N*-dicarbomethoxy-2,3-diazabicyclo[2.2.1]heptanes 17 and 18 from Alcohols 15 and 16. The preparation of **17** and **18** was accomplished by the reaction of either alcohol **15** or the mixture of alcohols enriched in **16** with sodium hydride and methyl iodide. The bromo alcohol (2.14 g; 6.7 mmol) was dissolved in a 50/50 mixture of dry ethyl ether and dimethylformamide and was cooled to 0 °C. Methyl iodide (2.82 g; 20 mmol) was added at 0 °C. To this, in small portions, was added excess sodium hydride (970 mg of a 57% oil dispersion; 20 mmol) which had been washed with pentane. The mixture was stirred for 2 h and allowed to warm to room temperature. Then water was carefully added. The solution was concentrated and then partitioned between ether and brine. The ether was dried over Na_2SO_4 and the solvent removed in vacuo. From **15** the product **17** was an oil: yield 2.13 g, 95%; NMR ($CDCl_3$) δ 6.42 (s, 1 H, vinyl H), 5.08 (s, 1 H, bridgehead), 4.80 (d, 1 H, bridgehead, J = 1 Hz), 3.84 (s, 7 H, CO_2CH_3 plus CHOR), 3.48 (s, 3 H, OCH_3), 2.30 (m, 1 H, endo H), 1.66 (m, 1 H, exo H). From the mixture enriched in **16**, the product was also an oil: yield 2.13 g, 95%. The NMR of the major methyl ether **18** is as follows: ($CDCl_3$) δ 6.34 (s, 1 H, vinyl H), 5.06 (d, 1 H, bridgehead, J = 1 Hz), 4.68 (s, 1 H, bridgehead), 3.90 (s, 7 H, CO_2CH_3 plus CHOR), 3.42 (s, 3 H, OCH_3), 2.30 (m, 1 H, endo H), 1.66 (m, 1 H, exo H). Molecular weight calcd for $C_{11}H_{15}N_2O_5Br$: 334.01648. Found for **18**: 334.01733. Found for **17**: 334.01899.

7-Methylene-5-exo-methoxy-*N*,*N*-dicarbomethoxy-2,3-diazabicyclo[2.2.1]heptane (19) from Methyl Ethers 17 and 18. To the mixture of methyl ethers **17** and **18** (230 mg; 0.7 mmol) in 10 mL of dry ethyl ether at −78 °C was added 1.25 mL of a *tert*-butyllithium solution (1.6 M in pentane, 2.1 mmol) at −78 °C. This was stirred for 1 h at −78 °C. To this was added 0.5 mL of absolute ethanol and 1 mL of water. The reaction was allowed to warm to room temperature and the product was partitioned between ether and water. The water layer was further extracted with ether, the combined ether layers were dried over Na_2SO_4, and the solvent was removed in vacuo. The crude product **19** was an orange oil which could be purified on 10 g of Florisil. Elution with ether and then ether/ethyl acetate (8:1) removed most aliphatic impurities resulting from contaminants contained in the *tert*-butyllithium. Elution with ether/ethyl acetate yielded 161 mg (90%) of a pale yellow oil: NMR ($CDCl_3$) δ 5.17 (s, 2 H, vinyl H), 4.63 (d, 1 H, bridgehead), 4.55 (s, 1 H, bridgehead), 3.80 (s, 7 H, CO_2CH_3 plus CHOR), 3.37 (s, 3 H, OCH_3), 2.30 (m, 1 H, endo H), 1.66 (m, 1 H, exo H).

7-*syn*-Deuteriomethylene-5-methoxy-*N*,*N*-dicarbomethoxy-2,3-diazabicyclo[2.2.1]heptane (19-*8-syn-d*) from Methyl Ether 17. Methyl ether **17** was reduced to carbamate **19**-*syn-d* following the above procedure. Ethanol-*d* and D_2O were substituted for ethanol and H_2O in the quenching step. The product **19**-*syn-d* was purified in the same fashion and showed the same NMR spectrum as **19** except that the intensity of the vinyl proton signal at δ 5.17 corresponded to only 1.1 H's.

Molecular weight calcd for $C_{11}H_{15}N_2O_5D_1$: 257.11224. Found: 257.11348.

7-Methylene-5-*exo*-methoxy-2,3-diazabicyclo[2.2.1]heptane. The methyl ether **19** (700 mg; 2.7 mmol) was dissolved in ether and added to a degassed solution of potassium hydroxide (920 mg; 16.4 mmol) in 25 mL of water. This was then heated to 85 °C and stirred overnight under nitrogen. The reaction was then cooled and 6 N HCl was added until the mixture was acidic and foaming occurred. Next potassium carbonate was added until the solution was saturated and the solution was extracted with chloroform which had been previously saturated with nitrogen. The chloroform was dried over Na_2SO_4 and the solvent removed in vacuo. The product hydrazine was an unstable yellow oil: 356 mg, 94% yield; NMR ($CDCl_3$) δ 5.12 (s, 2 H, methylene H), 3.55 (d, 1 H, bridgehead, J = 1 Hz), 3.50–3.40 (m, 4 H, bridgehead, plus NH, plus CHOR), 3.38 (s, 3 H, OCH_3), 2.20 (m, 1 H, endo H), 1.67 (m, 1 H, exo H).

7-*syn*-Deuteriomethylene-5-*exo*-methoxy-2,3-diazabicyclo[2.2.1]heptane. The carbamate **19**-*8-syn-d* was hydrolyzed following the same procedure. The product from the hydrolysis was an unstable oil which possessed the same NMR spectrum as the above hydrazine except that the intensity of the vinyl proton signal at δ 5.12 corresponded to only 1.1 H's.

7-Methylene-5-*exo*-methoxy-2,3-diazabicyclo[2.2.1]hept-2-ene (20). The hydrazine (356 mg; 2.5 mmol) was dissolved in 80 mL of acetone and to it was added oxygen gas, bubbled through a glass tube. The oxidation was run for 2 h. The acetone was removed in vacuo and the oil dissolved in ether. The ether solution was filtered through Celite 545 and the ether removed in vacuo. The azo compound was a yellow oil which could be purified by elution from 10 g of Florisil with ethyl ether: NMR ($CDCl_3$) δ 5.44 (s, 1 H, bridgehead), 5.28 (d, 1 H, bridgehead, J = 1 Hz), 5.06 (d, 2 H, methylene H, J = 2 Hz), 3.44 (s, 4 H, CHOR plus OCH_3), 1.60 (m, 2 H, CH_2).

7-*syn*-Deuteriomethylene-5-*exo*-methoxy-2,3-diazabicyclo[2.2.1]hept-2-ene (20-*8-syn-d*). The hydrazine was oxidized to the corresponding azo compound following the same procedure. The product from the oxidation was a yellow oil which was purified in the same fashion as **20** and which possessed the same NMR as **20** except for the diminished intensity of the vinyl absorptions (1.1 H's instead of 2 H's).

Photolysis of Diazene 20 in Cyclopentadiene. A solution of 40 mg (0.16 mmol) of diazene **20** in 300 μL of neat cyclopentadiene was placed in a Pyrex tube, degassed and sealed, and photolyzed at 0 °C for 8 h in the Rayonet with 16 lamps (350 nm). The reaction tube was opened and the excess cyclopentadiene removed in vacuo. The residue was analyzed first on column A at 125 °C and the products were separated preparatively on column B at 134 °C. Each component was further analyzed on column C at 55–65 °C and fractionated preparatively on column D. The details of the isolation and characterization of the products are given elsewhere.[15] Figure 1 shows the dependence of the product distribution on the initial concentration of cyclopentadiene.

When the same reaction was carried out with 80 mg of **20**-*8-syn-d* (containing 0.8 D/molecule) in 600 μL of cyclopentadiene and the bridged adducts **31–35** separated as before, the intensities of the geminal $=CH_2$ proton resonances were identical in each case, and their sum amounted to 1.2 units.[15]

Control Experiments. Photolysis of Diazene 20 in Perdeuteriocyclopentadiene. A solution of 20 mg (0.08 mmol) of diazene **20** in ~0.75 mL of perdeuteriocyclopentadiene[34] was placed in an NMR tube, degassed, and sealed. The ^1H NMR spectrum (probe at 0 °C) of the starting solution clearly showed the signals due to the exocyclic methylene protons of **20**. These appear at δ 5.06 in deuteriochloroform. The photolysis was followed by comparing the size of this signal to the vinyl region observed for the small percentage of protiocyclopentadiene in the perdeuterated solvent.

After the solution was photolyzed for 1 h (0 °C, sixteen 350-nm lamps), the ^1H NMR indicated that only about one-half of the starting compound **20** remained. After 2.5 h of irradiation, no signal attributable to the starting azo compound **20** could be observed.

This solution was subjected to analytical VPC on column A and the percentages of the cycloadducts observed were identical, within experimental error, with those obtained for the photolysis of **20** at 0 °C in neat protiocyclopentadiene.

On the basis of these observations, it was concluded that 8 h of irradiation (0 °C, sixteen 350-nm lamps) was more than sufficient to decompose all of the diazene. Although a mass balance determination was not carried out, the azo compound **20** appears to have undergone essentially 100% conversion to cycloadducts and dimers.

Stability of the Cycloadducts to the Reaction Conditions in the Photolysis of Diazene 20 in Cyclopentadiene. Three photolysis tubes, each containing ~20 mg (0.08 mmol) of diazene **20** in 150 μL of neat cyclopentadiene, were degassed and sealed. The tubes were then irradiated at 0 °C using 16 lamps (350 nm) each for a different length of time. Tube no. 1 was irradiated for 2 h, tube no. 2 for 4 h, and tube no. 3 for 8 h. The tubes were opened and the excess cyclopentadiene removed in vacuo. The residues were each analyzed on column A at 125 °C to see if any gross changes in the product distribution could be detected from one sample to the next. The gas chromatograms were virtually superimposable. Therefore, under the typical reaction conditions the cycloadducts are stable.

Check for Deuterium Label Scrambling in the Unreacted Azo Compound during the Photolysis of Diazene 20-*8-syn-d* in Cyclopentadiene. Three photolysis tubes, each containing ~20 mg (0.08 mmol) of diazene **20**-*8-syn-d* in 150 μL of neat cyclopentadiene, were degassed and sealed. The tubes were then irradiated at 0 °C using 16 lamps (350 nm) each for a different length of time. Tube no. 1 was irradiated for 15 min, tube no. 2 for 30 min, and tube no. 3 for 60 min. The tubes were then opened and the excess cyclopentadiene removed in vacuo. The residues were each dissolved in $CDCl_3$ and transferred into NMR tubes. NMR's at 270 MHz were taken of the three samples and the region where the *exo*-methylene (~δ 5.0) absorptions appeared and was examined. Each sample had some quantity of unphotolyzed azo compound remaining and

in each case the methylene absorption had the same distribution of proton and deuterium in the 7-methylene position as the starting azo compound (which had a deuterium incorporation of 90% and a ratio of the *exo*-methylene proton signals of 1.0/0.1).

Photolysis of Diazene 20 at −78 °C. A solution of ~20 mg (0.08 mmol) of diazene **20** in 0.75 mL of $CDCl_3/CFCl_3$ was placed in an NMR tube, degassed, and sealed. The tube was suspended in an unsilvered Dewar containing a dry ice/ethanol (−78 °C) slush and photolyzed for 2 h with 16 lamps (350 nm). The tube was then transferred, without warming, into the probe of the HX270 NMR spectrometer which had been precooled to −78 °C. The NMR spectrum of the crude photolysate revealed that the starting diazene had been totally consumed and had given way to two new compounds (as evidenced by the presence of only two sharp –OMe singlets at δ 3.24 and 3.37), in a ratio of 3:1, respectively. Warming of the NMR probe to −60 °C initiated the conversion of the minor product into the major product with $t_{1/2} \simeq 30$ min. Further warming of the NMR probe to +10 °C initiated the disappearance of the major product into several different compounds with $t_{1/2} \simeq 20$ min. The NMR spectrum of the final products was very similar to that of dimers of **25**. A GC/MS of the products proved to be identical with that found for the dimers produced during the 0 °C photolysis of diazene **20** in neat cyclopentadiene. The mass spectrum showed prominent peaks at *m/e* 220 (parent), 156, 129, 128, 115, 32 (base).

The NMR spectrum of the major photolysis component, **46**, is as follows: δ 5.35 (d, 2 H, exo methylene protons, $J = 3$ Hz), 4.13 (m, 1 H, α to OCH_3), 3.24 (s, 3 H, OCH_3), 2.55 (m, 1 H, endo proton on ethano bridge), 2.49 (m, 1 H, bridgehead β to OCH_3), 2.14 (m, 1 H, other bridgehead proton), 1.65 (d × d, 1 H, exo proton on ethano bridge, $J = 11$ and 3 Hz). The NMR spectrum of the minor component, **47**, is as follows: δ 5.25 (d, 2 H, exo methylene protons, $J = 11$ Hz), 3.61 (d × d, 1 H, α to OCH_3, $J = 5$ and 1 Hz), 3.37 (s, 3 H, OCH_3), 2.43 (d, 1 H, bridgehead proton), 2.34 (m, 1 H, bridgehead proton), 2.11 (m, 1 H, exo proton on ethano bridge), 2.09 (m, 1 H, endo proton on ethano bridge).

Effect of Eu(fod)$_3$ on NMR Spectra of 46 and 47. A solution of ~5 mg (0.02 mmol) of diazene **20** in 0.75 mL of $CDCl_3/CFCl_3$ was placed in an NMR tube and a serum cap placed atop the tube. The tube was flushed for 15 min with dry N_2 gas via a syringe needle attached to a N_2 source and vented through a second syringe needle. The sample was then photolyzed in an unsilvered Dewar at −78 °C (ethanol/dry ice) for a period of 2 h with 16 lamps (350 nm). The tube was then transferred to the precooled NMR probe (−75 °C) and an NMR spectrum taken of the two [2.1.0] isomers (see previous experiment for NMR data).

A solution of 0.28 g of Eu(fod)$_3$ in 1 mL of $CDCl_3/CFCl_3$ (1:1) was then prepared. Successive additions of 10 μL of the 0.27 M Eu(fod)$_3$ were made via a Hamilton syringe to the cold sample and an NMR spectrum taken after each addition at −75 °C (an equilibration time of 30–40 min at −75 °C in the NMR probe was necessary before the NMR spectrum could be taken). Additions of the Eu(fod)$_3$ solution were ceased when no further changes in the NMR spectrum could be realized. Typically between 40 and 70 μL were added before no further changes could be seen. In general, all the absorptions in the NMR spectrum broadened and shifted downfield slightly. The resonances of particular interest were the exo methylene absorptions of both the major and minor isomers. The center of the methylene resonances of the major isomer shifted from δ 5.35 to 5.45 with respect to $CHCl_3$ at δ 7.27. The methylene doublet of the minor isomer shifted from δ 5.25 to 5.27. Warming of the NMR probe to −30 °C initiated the conversion of the minor isomer into the major one and also considerably sharpened the NMR signals. The methylene doublet of the major isomer was now positioned at δ 5.53 and was resolved nearly to base line. Further warming of the NMR probe to −5 °C caused the decomposition of the compound with $t_{1/2} \simeq 15$ min.

Proton Decoupling NMR Analysis of Compounds 46 and 47. Complete proton decoupling NMR analyses were done on both of the bicyclic hydrocarbons **46** and **47** at −78 °C with the 270-MHz spectrometer. The data are presented in condensed, graphic form indicating the proton or protons decoupled and the respective changes to the absorptions of the remaining, undecoupled protons. (A blank space indicates no change and a – indicates the proton or protons decoupled, Table II.)

Photolysis of Diazene 20 at −78 °C and at −196 °C in Toluene-d_8. Two solutions of ~8 mg (0.032 mmol) of **20** in 0.75 mL of toluene-d_8 were prepared. They were added to NMR tubes which were degassed and sealed. One tube was photolyzed for 2 h at −78 °C (ethanol/dry ice) with 16 lamps (350 nm). The other tube was photolyzed for 2 h at −196 °C (liquid N_2), as a cracked glass, with 16 lamps (350 nm). The NMR spectrum (−75 °C) at 270 MHz of the crude photolysate from the −78 °C photolysis revealed exclusive formation of the two isomeric [2.1.0] compounds **46** and **47** in a ratio of 3:1. Noteworthy is the fact that in toluene-d_8, the methylene absorptions of both the major and minor isomers were nearly base line resolved pairs. The NMR spectrum (−75 °C) at 270 MHz of the photolysate from the −196 °C photolysis showed that only ~20% of the reaction mixture was comprised of the isomeric [2.1.0] compounds **46** and **47**. The remaining 80% was a complex mixture of at least 15 compounds whose NMR spectrum matched that of the TMM dimers produced from the decomposition of [2.1.0] compound **47** at +5 °C. Gradual warming of the NMR probe to +5 °C produced the thermal decomposition of both [2.1.0] compounds to dimers, but no changes other than signal enhancement of the TMM dimer absorptions in the NMR could be seen.

Table II. Spin Decoupling of ^{1}H NMR Spectra of 46 and 47

Compound 46 (major)

Decoupler offset (ppm)

Proton chemical shift (ppm), count, and multiplicity

	a	5.35	4.13	3.24	2.55	2.49	2.14	1.65
5.35 2H	d	-						
4.13 1H	m		-		dxd	dxd		dxd
3.24 3H	s			-				dxd
2.55 1H	m		m		-		dxd	
2.49 1H	m		m			-	m	
2.14 1H	m				m	m	-	
1.65 1H	dxd		d		d			-

Compound 47 (minor)

	a	5.25	3.61	3.37	2.43	2.34	2.11	2.09
5.25 2H	d	-						
3.61 1H	dxd		-				d	d
3.37 3H	s			-				
2.43 1H	d				-	s		
2.34 1H	m				m	-		m
2.11 1H	dxd		d				-	d
2.09 1H	m		dxd			dxd	dxd	-

*Multiplicity before decoupling

Photolysis of Diazene 20 at −110 °C in $CFCl_3$. A solution of ~8 mg (0.032 mmol) of azo compound **20** in 0.75 mL of $CFCl_3$ was placed in an NMR tube which was degassed and sealed. The tube was photolyzed at −110 °C (cooled N_2 gas) for 2 h with 16 lamps (350 nm). An NMR spectrum (−75 °C) at 270 MHz showed that ~90–95% of the crude photolysate was comprised of the two isomeric [2.1.0] compounds **46** and **47**. The other 5–10% was a complex mixture of what appeared to be TMM dimers of diyl **25**. Gradual warming of the NMR probe to +5 °C initiated the conversion of the [2.1.0] compounds into the compounds comprising the initial 5–10% of the crude photolysate.

Kinetics. The thermal reactions of **46** and **47** were followed with the Bruker HX 270 NMR system, using essentially the same techniques described elsewhere.[6] Conversion of the minor isomer (**47**) of the 2-methoxy-5-methylenebicyclo[2.1.0]pentanes to the major one (**46**) in $CDCl_3/CFCl_3$ was followed by observing the disappearance of the δ 5.25 NMR signal of **47** relative to the $CHCl_3$ singlet at δ 7.27. The observed first-order rate constants (×10^4 s), temperatures (K), and correlation coefficients were: 1.11, 209.99, 0.987; 2.99, 215.31, 0.995; 8.11, 223.66, 0.985.

Conversion of the major isomer (**46**) to dimers in $CDCl_3/CFCl_3$ solution (initially ca. 0.2 M) was monitored by observation of the ratio of the δ 5.35 NMR signal intensity to that of the $CHCl_3$ internal standard. A typical set of data obtained at 271.91 K for the absorption ratio vs. time in minutes was: 0.626 (0), 0.551 (15), 0.477 (30), 0.368 (45), 0.364 (60), 0.300 (75), 0.271 (90). The following values of the first-order rate constant (×10^4 s), temperatures (K), and correlation coefficients were obtained: 1.59, 271.91, 0.996; 2.29, 275.06, 0.998; 7.31, 283.69, 0.978; 9.60, 289.36, 0.994. The Arrhenius parameters were $E_a = 16.9$ kcal/mol, $\log A = 9.8$ (A in s).

In a control experiment to check for the possibility of trace metal catalysis, a sample of diazene **20** in $CDCl_3/CFCl_3$ was washed with 1 M disodium ethylenediaminetetraacetate (EDTA)/D_2O solution before being transferred to an oven-dried NMR tube that had been prewashed with EDTA solution. Photolysis in the usual manner gave a solution of **46** which was pyrolyzed at 284.95 K. The rate constant ×10^4 s was 6.22,

which was within experimental error of the value predicted (6.9) by interpolation from the Arrhenius parameters.

Reaction of Endo and Exo [2.1.0] Isomers 46 and 47 with Cyclopentadiene. A solution of 80 mg (0.32 mmol) of diazene **20** in 0.75 mL of $CDCl_3/CFCl_3$ (1:1) was placed in a 5-mm Pyrex photolysis tube, which was flushed with N_2 gas and capped with a serum cap, and photolyzed for 2 h at −78 °C with 16 lamps (350 nm). After the photolysis was complete, 5 mL of neat, freshly cracked cyclopentadiene (precooled to −78 °C) was added. The reaction mixture was then placed into an ice/water bath and allowed to sit at 0 °C for 8 h in the dark. The cyclopentadiene was then removed in vacuo and the crude material analyzed on the analytical gas chromatograph at 125 °C using column A. The gas chromatogram which resulted was essentially superimposable on one taken previously of the crude photolysate of diazene **20** in neat cyclopentadiene at 0 °C.

Reaction of the Syn [2.1.0] Isomer 46 with Cyclopentadiene at 0 °C. A solution of 80 mg (0.32 mmol) of diazene **20** in 0.75 mL of $CDCl_3/CFCl_3$ (1:1) was placed in an NMR tube, which was flushed with N_2 gas and capped, and photolyzed for 1.5 h at 0 °C with 16 lamps (350 nm). After the photolysis was complete, an NMR spectrum (−10 °C) was taken of the crude photolysate. The NMR revealed the presence of only the syn [2.1.0] isomer **46**. To this solution was added 5 mL of neat, freshly prepared cyclopentadiene (precooled to 0 °C). The mixture was allowed to stand at 0 °C, in the dark, for 8 h. The cyclopentadiene was then removed in vacuo and the crude material analyzed on the analytical gas chromatograph at 125 °C using column A. The gas chromatogram which resulted was essentially superimposable on the one taken of the crude photolysate from photolysis of diazene **20** in neat cyclopentadiene at 0 °C.

Photolysis of Deuterated Diazene 20-*8-syn-d* at −78 °C. Two solutions, one containing 20 mg (0.32 mmol) of diazene **20-*8-syn-d*** in 0.75 mL of $CDCl_3/CFCl_3$ (1:1) and one in 0.75 mL of toluene-d_8, were prepared. They were placed in separate NMR tubes, which were flushed with N_2 gas and capped, and each was photolyzed for 2 h at −78 °C with 16 lamps (350 nm). NMR spectra of the two solutions (at −75 °C) show the presence of the endo and exo isomers **46-*d*** and **47-*d***. Addition of 70 μL of an Eu(fod)$_3$ solution (0.27 M in $CFCl_3/CDCl_3$, 1:1) to the $CFCl_3/CDCl_3$ sample resulted in resolution of the individual exocyclic methylene proton resonances of both isomers. In toluene-d_8 (at −90 °C) the exocyclic methylene resonances were discernible without the aid of the lanthanide shift reagent. In both solvents, both isomers showed partial stereochemical scrambling of the deuterium to the same extent. The ratio of the exocyclic methylene resonances in each case was 2.0. Raising the temperature to −60 °C initiated the conversion of the minor isomer **47** into the major one with no further scrambling of the deuterium label in the minor isomer **47**, or the major isomer **46**, being apparent. Further warming to −40 °C caused the deuterium label in the major isomer **46** to undergo syn/anti scrambling with $t_{1/2} \simeq 15$ min. In both solvents the rate of scrambling was approximately the same. Finally, as the temperature was raised to +5 °C, dimerization was apparent.

Determination of the Rate Constant for Deuterium Label Scrambling in the Endo [2.1.0] Isomer 46-*d* at −45 °C in $CDCl_3/CFCl_3$ (1:1). To check for the effect of Eu(fod)$_3$ on the rate of deuterium label scramblings, two samples, each containing ~20 mg (0.08 mmol) of azo compound **20-*8-syn-d*** in 0.75 mL of $CDCl_3/CFCl_3$ (1:1), were prepared. They were placed in NMR tubes, which were flushed with N_2 gas and capped, and photolyzed for 2 h at −78 °C with 16 lamps (350 nm). To one tube was added 70 μL of 0.27 M Eu(fod)$_3$ in $CDCl_3/CFCl_3$ (1:1) solution (precooled to −78 °C). The sample was then placed into the NMR probe which was cooled to −45 ± 1 °C and the sample was allowed to equilibrate for 20 min. The NMR spectrum showed that the ratio of the downfield methylene signal, which corresponds to the absorption due to the proton anti to the OMe, to the sum total of both methylene signals was 0.449.

The other sample was placed into the NMR probe for 22 min at −45 °C and then quickly cooled to −78 °C by immersion into a dry ice/acetone bath. Then, to this tube, was added 70 μL of the same 0.27 M Eu(fod)$_3$ solution. An NMR spectrum (at −75 °C) of this sample showed the ratio of the downfield methylene to the sum of the methylenes to be equal to 0.447. This ratio is the same, within experimental error, as that observed for the scrambling process that occurred in the presence of Eu(fod)$_3$. It seems, therefore, that the lanthanide shift reagent has little effect on the rate of syn/anti deuterium scrambling.

A similar experiment showed that the half-life for scrambling of the label at −40 °C in toluene-d_8 solution was between 15 and 20 min. This corresponds to $k \times 10^4$ s = 5.7–7.7.

Reaction of Syn and Anti [2.1.0] Isomers 46-*d* and 47-*d* with Cyclopentadiene. A solution of 80 mg (0.32 mmol) of diazene **20-*8-syn-d*** in 0.75 mL of $CDCl_3/CFCl_3$ (1:1) was placed in an NMR tube, which was flushed with N_2 gas and capped, and photolyzed for 2 h at −78 °C with 16 lamps (350 nm). After the photolysis was complete, an NMR spectrum was taken of the crude photolysate at −75 °C. The NMR revealed the bicyclo[2.1.0] pentane isomers **46-*d*** and **47-*d*** to be present with the deuterium label only partially scrambled (as described earlier). To this solution was added 5 mL of neat, freshly prepared cyclopentadiene (precooled to −78 °C). The reaction mixture was placed in an ice/water bath and allowed to sit at 0 °C for 8 h in the dark. The cyclopentadiene was then removed in vacuo and the crude material analyzed on the analytical gas chromatograph at 125 °C using column A. The gas chromatogram was virtually superimposable to one taken previously of the crude photolysate from diazene **20** in neat cyclopentadiene at 0 °C. Isolation of the individual adducts and NMR analyses at 270 MHz of each cycloadduct revealed the deuterium label to be completely scrambled in each compound.

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Registry No. 13, 68241-85-0; **14**, 80963-57-1; **15**, 72448-10-3; **16**, 81025-22-1; **17**, 81026-57-5; **18**, 80975-51-5; **19**, 80963-58-2; **19-*syn-d***, 80963-59-3; **20**, 72447-93-9; **20-*syn-d***, 72448-07-8; **28**, 60743-11-5; **29**, 75156-46-6; **30**, isomer 1, 75156-48-8; **30**, isomer 2, 75156-49-9; **46**, 72447-91-7; **47**, 72447-90-6; **103**, 80963-60-6; **104**, 81024-54-6; **107**, 80963-61-7; **108**, 80963-62-8; **109**, 80963-63-9; **110**, 80963-64-0; **111**, 80963-65-1; **113**, 80963-66-2; **133**, 80963-67-3; **134**, 81024-55-7; **135**, 81024-56-8; **136**, 81024-57-9; dimethyl azodicarboxylate, 2446-84-6; cyclopentadiene, 542-92-7.

Supplementary Material Available: Descriptions of isolation, elemental composition, and spectroscopic properties of **31A–39** (Scheme V), **40**, and **41** (22 pages). Ordering information is given on any current masthead page.