it appears here.
(14) For an alternate synthesis and thermolysis of *cis*- and *trans*-cyclobutane-*1,2-d*$_2$, see ref 7j.
(15) This reaction has been shown to be 95% stereospecific inversion for secondary centers, i.e., *threo*-3-methyl-1,4-pentanediyl 1,4-dimethanesulfonate affords dimethyl *cis*-3,4-dimethyltetrahydropyridazine-1,2-dicarboxylate and *erythro*-dimethanesulfonate affords trans 3,4-disubstituted diurethanes.[9e]
(16) Perkin-Elmer Model 180 infrared spectrophotometer. We thank Dr. George Rossman, Division of Geological and Planetary Sciences, California Institute of Technology, for allowing us to use this instrument.
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Regioselectivity in Cycloadditions of Singlet 2-Methylenecyclopenta-1,3-diyl Species[1]

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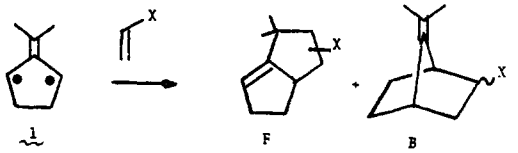
Abstract: The regioselectivity for fused adduct in the cycloaddition of singlet 2-methylenecyclopenta-1,3-diyls to olefins can be explained either as an orbital overlap effect in a reaction of a bisected singlet trimethylenemethane (TMM) or as an orbital symmetry effect in a reaction of a planar singlet TMM. The first hypothesis predicts the same regioselectivity in 1,2 and 1,4 cycloadditions to conjugated dienes (fused adducts), but the second hypothesis predicts a switch in regioselectivity, in which 1,2 addition should give fused adduct and 1,4 addition should give bridged adduct. In the latter case, a further prediction of the orbital symmetry model is that the adduct with the syn relationship between the exocyclic double bond and the newly developing ring double bond should be favored over its anti isomer. The predictions of the orbital symmetry model are confirmed in every instance in the cycloaddition of 2-methylenecyclopenta-1,3-diyl to cyclopentadiene. The dominant products are fused 1,2 and syn-bridged 1,4 adducts.

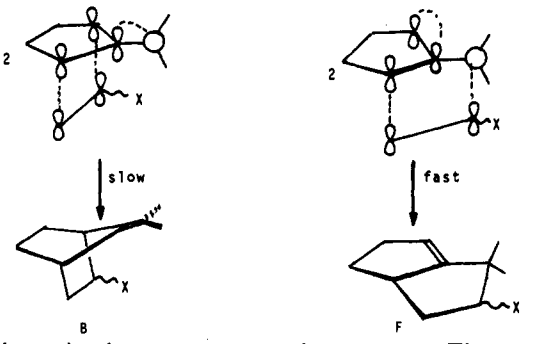
The trimethylenemethane (TMM) biradical 2-isopropylidenecyclopenta-1,3-diyl (**1**) reacts with olefins to give [3 + 2] cycloadducts[3] by pathways involving two mechanistically distinguishable forms, a singlet and a triplet.[4] Such cycloadditions should be capable of forming both fused (F) and bridged (B) adducts, a prediction verified by experience[4] with the *triplet* diyl **1**. This species gives F and B with little or no



preference for either. It is therefore remarkable that the cycloadditions of the *singlet* are highly regioselective and give largely the fused isomer.[4]

Our first attempt[4] to rationalize the behavior of the singlet invoked the bisected TMM **2** as the reactive species. Theory[5] suggests that in the singlet manifold the bisected configuration should be readily accessible by twisting one methylene group of TMM out of the plane of the other two. Moreover, there is ample experimental support for the occurrence of this process.[6] From the strict syn stereoselectivity of the singlet cycloaddition, we also infer that the singlet + olefin reaction probably is concerted. Concerted reaction at the potential bridgehead sites (**2** → B) generates a twisted π bond in the transition state, whereas reaction at one ring site and the exocyclic site (**2** → F) does not. This would tend to retard the formation of bridged cycloadduct.

An alternative rationale for regioselective formation of fused adduct can be constructed on the basis of orbital-symmetry[7] relationships in the diyl and diylophile. Frontier orbital theory[8]



provides a simple way to present the argument. Thus, a concerted, orbital symmetry allowed cycloaddition could occur only at the TMM sites at which the orbital phase properties of the TMM's highest occupied molecular orbital (HOMO) match those of the olefin's lowest unoccupied MO (LUMO), normally the antisymmetric π^* MO.

The TMM's HOMO must be one of the two nominally degenerate nonbonding orbitals **3**-S or **3**-A (Figure 1),[9] since four electrons must be accommodated in the π system. In a planar TMM, these MOs are truly degenerate at the level of simple Hückel theory, even when, as in **1**, the D_{3h} structure of the parent compound is distorted to C_{2v}. We defer a discussion of more sophisticated theory which rationalizes a splitting of the degenerate Hückel MOs, and for the purpose of argument we examine the corollaries of the hypotheses that the *reactive* singlet is planar, that the S level is below the A by a large enough gap to make S the HOMO, and that the regioselectivity of cycloaddition is frontier orbital controlled. The ordering S below A is chosen to make the hypothesis conform to the experimentally observed regioselectivity.

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Table I. Orbital Phase Relationships in the Formation of Bridged and Fused Olefin Adducts When Diyl HOMO is **1-S**

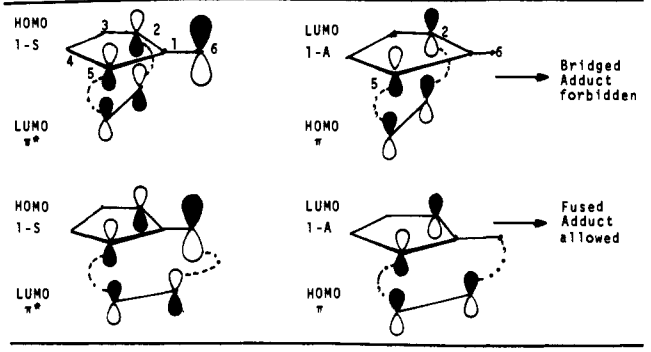
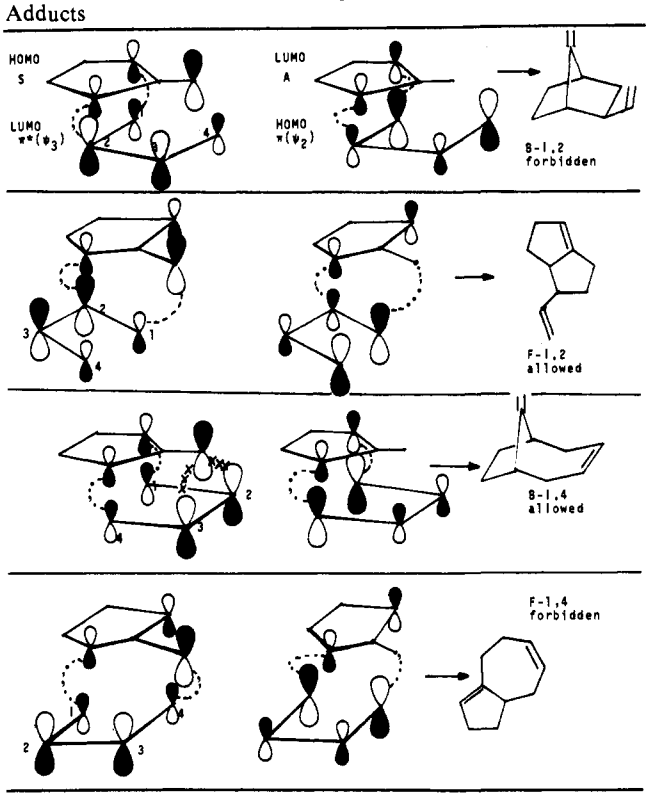


Table II. Orbital Phase Relationships in the Formation of Diene Adducts



In the C_{2v} symmetry imposed by the structure **1**, the exocyclic carbon of the TMM system plays the role of the unique methylene carbon. The HOMO (**1**-S) therefore has the in-phase π orbital relationship at the ring carbons, C-2 and C-5, and the out-of-phase reationship at C-2 (or C-5) and the exocyclic position C-6, whereas the LUMO (**1**-A) is out of phase at C-2–C-5 and has a node at C-6 (Table I). Bridged adduct formation therefore is disfavored by both diyl HOMO–olefin LUMO and diyl LUMO–olefin HOMO interactions, but fused adduct formation is favored by both. Clearly, if the HOMO–LUMO ordering for diyl **1** were inverted (A below S), bridged adduct would be favored, which conflicts with experiment.

Extension of this hypothesis to the cycloadditions of conjugated dienes and singlet diyl **1** suggests a further experimental test. Table II shows the orbital phase relationships for addition at C-1–C-2 and at C-1–C-4 of a *conjugated diene.* The 1,2 addition should favor fused adduct, just as in the monoolefin case, because the phase properties of the C-1–C-2 sites of the diene's HOMO and LUMO are just the same as those of the olefin. However, the 1,4 addition should favor *bridged* adduct because of the orbital phase inversion at C_4 relative to

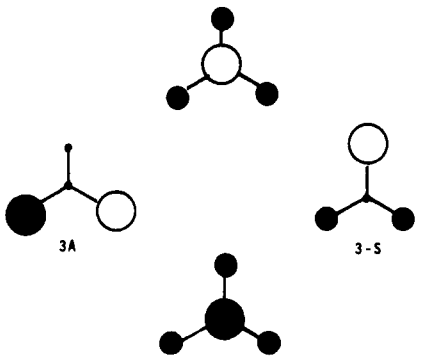


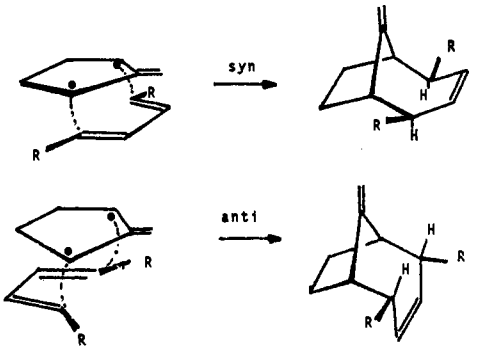
Figure 1. Orbital phase properties of the TMM π system from simple Hückel theory.[9]

C_2 of the diene's HOMO and LUMO. This predicted switch in regioselectivity offers the possibility of a clear decision between the orbital symmetry rationale and the earlier bisected singlet hypothesis. The twisted π bond in the transition state for bridged adduct formation would be present in both 1,2 and 1,4 cycloaddition to the bisected singlet. One therefore would not expect a switch in regioselectivity between 1,2 and 1,4 cycloaddition in that case.

The electron densities at the reactive sites in the frontier orbitals involved in the F-1,2 and B-1,4 reactions are not identical, and hence some regioselectivity for one of the two allowed modes might be expected. As we shall see, experimentally the F-1,2 path predominates, but, since there is a statistical factor of 2 in favor of fused vs. bridged addition to a diene, and since the steric requirements of the two processes are different and not readily quantifiable, it does not seem fruitful to speculate on how much of the preference should be ascribed to the frontier MO electron density differences.

Within the F-1,2 series, there are two regioisomers, each of which can be formed in either of two stereoisomeric forms by a suprafacial–suprafacial cycloaddition. Frontier orbital interactions do not suggest a pronounced stereoisomeric preference, and regioisomeric preferences do not appear to be strong. The F-1,2 product therefore might well appear as a mixture.

However, the frontier MO model does predict a rather pronounced preference for one of the two stereochemically possible modes of B-1,4 addition that become discernible in appropriately substituted systems. The transition-state orientation leading to an adduct with a syn relationship between the exocyclic and endocyclic double bond has an in-phase stabilizing secondary orbital interaction (shown by xxx in Table II) between the exocyclic carbon orbital of the diyl HOMO and the C-2 and C-3 orbitals of the diene LUMO. This interaction is sacrificed in the anti orientation. The syn and anti modes are analogous electronically to the endo and

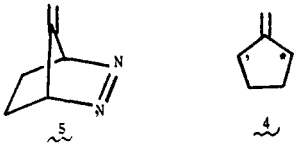


exo modes, respectively, of Diels–Alder reactions, where the preference for endo addition has been rationalized[7,8,10] by similar secondary orbital interactions.

Table III. Predictions of the Bisected Singlet and Orbital Symmetry Hypotheses for Reactions of Singlet 2-Alkylidenecyclopenta-1,3-diyl (1)

model	predicted diene adduct	
	1.2	1.4
bisected singlet	F	F
orbital symmetry		
HOMO S-LUMO A	F	*syn*-B
HOMO A-LUMO S	*syn*-B	F

Table III summarizes the predictions of the contending models. In designing experimental tests of the predictions, it is desirable to minimize steric effects so that the underlying electronic features of the two hypotheses can be examined. For this reason, we have chosen to work with the parent 2-methylene cyclopenta-1,3-diyl **4** rather than the 2-isopropylidene compound **1**. The next section describes syntheses of 7-methylene-2,3-diazabicyclo[2.2.1]hept-2-ene (**5**), the precursor of



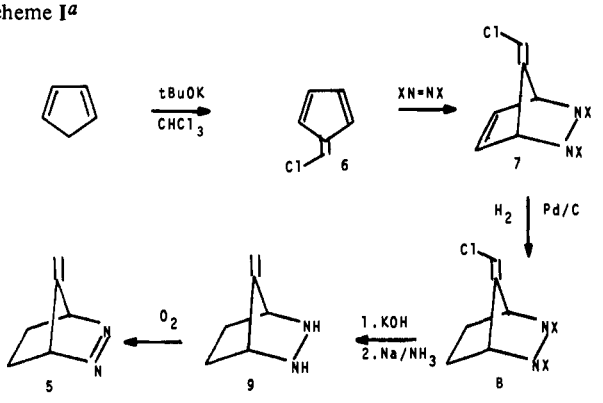
4. Readers to whom these details are of secondary interest may pick up the thread of the mechanistic studies by skipping to the section headed "Reactions of Diazene".

Synthesis of 7-Methylene-2,3-diazabicyclo[2.2.1]hept-2-ene (5). Diazene **5** had been synthesized[11] by the route shown in Scheme I. 6-Chlorofulvene (**6**), available in low yield (~10%) from the action of sodium cyclopentadienide on chloroform by the method of D'Amore and Bergman,[12] gave the Diels–Alder adduct **7** when allowed to react with dimethyl azodicarboxylate. Selective hydrogenation of **7** gave the reduced carbamate **8**, which by consecutive basic hydrolysis, reductive dehalogenation, and oxidation was converted in good yield to the desired diazene **5**. Although this sequence was short, it suffered from the severe limitation that the starting material **6** was not conveniently available in quantity.

We now have worked out two alternative procedures to alleviate this problem. Both of these syntheses were designed to achieve high selectivity for the ring double bond in the semihydrogenation step, a goal that probably could not have been reached had the exocyclic double bond terminated in an unsubstituted methylene group.

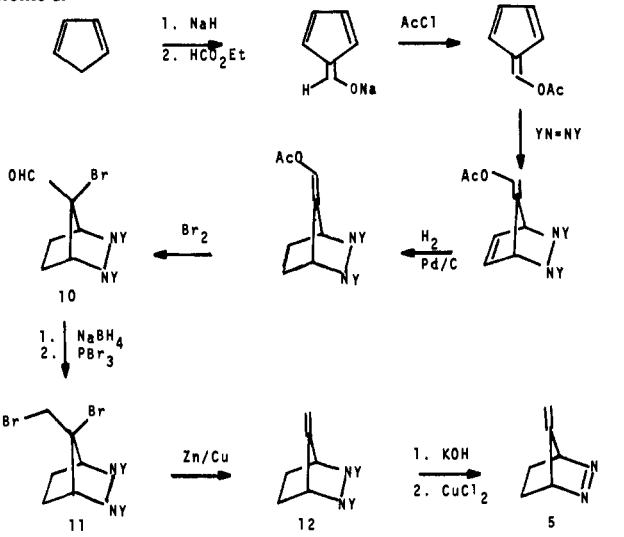
One of the new syntheses (Scheme II) started with cyclopentadiene and proceeded via 6-acetoxyfulvene,[13] which was converted by the procedure of Trost and Cory[14] to the bromo aldehyde **10** (configuration arbitrary). The five steps indicated in Scheme II for the transformation of **10** to the diazene **5** all were effected in high yield, and the overall yield of **5** from cyclopentadiene by the entire ten-step sequence was 32%. The pure diazene **5** was obtained as a low-melting, white, crystalline solid which was unstable in the homogeneous state but could be stored in chloroform solution over solid potassium carbonate at −40 °C.

Scheme I[a]



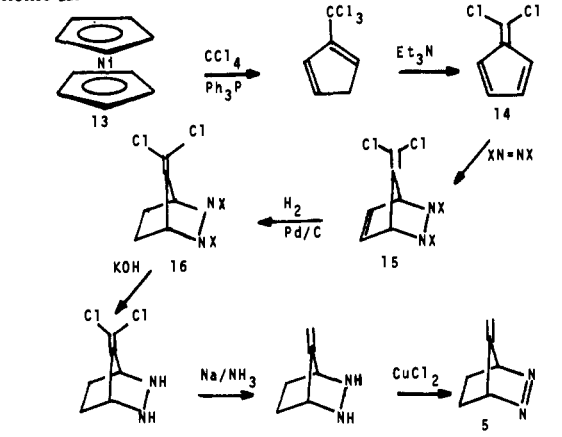
[a] X = CO_2Me.

Scheme II[a]



[a] Y = CO_2Et.

Scheme III[a]



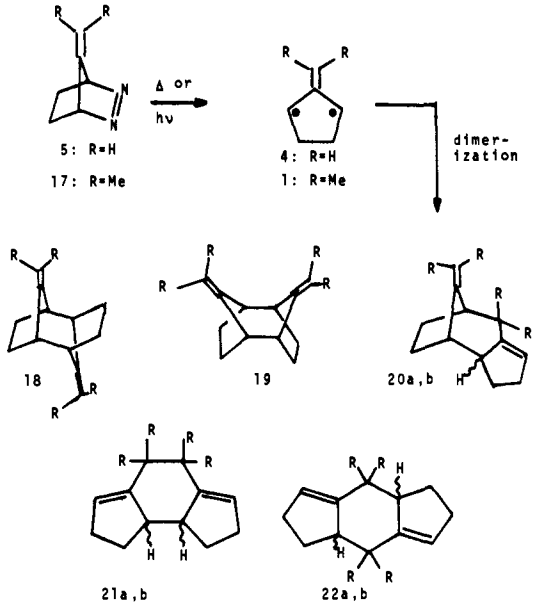
[a] X = CO_2Me.

A shorter sequence (Scheme III) started with 6,6-dichlorofulvene (**14**), available from nickelocene **13** by a modification of the method of Moberg and Nilsson.[15] The unsaturated dichlorocarbamate **15** was obtained in 60–65% overall yield from nickelocene and could be carried through the remaining five-step sequence in yields approaching 70%.

Reactions of the Diazene 5. TMM Dimers. Like the 7-isopropylidene analogue **17**,[4c,16] 7-methylene-2,3-diazabicyclo[2.2.1]hept-2-ene (**5**) loses nitrogen thermally or photochemically and gives a series of dimers of the corresponding TMM. Eight dimeric products are possible in principle from the TMM (Scheme IV). From the pyrolysis (60 °C) of ether or acetonitrile solutions of the methylenediazene **5**, we now have isolated five of these by preparative gas chromatography (GC) and characterized them by their spectroscopic properties.

Each dimer showed a mass spectrometric parent peak at *m/e* 160, corresponding to the empirical composition $C_{12}H_{16}$. The structures were established by the ^{13}C and proton nuclear magnetic resonance (NMR) spectra, which are detailed in the Experimental Section. About 22% of the reaction mixture consisted of one of the fused-bridged dimers **20a,b** (R = H). The ^1H NMR spectrum of this fraction showed a singlet at δ

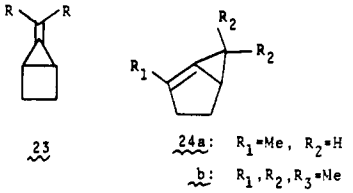
Scheme IV. Possible Dimers of 2-Alkylidenecyclopenta-1,3-diyls



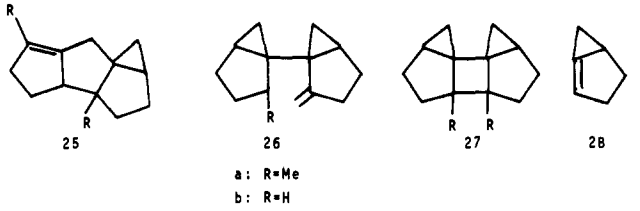
4.75 (2 H) and a broad singlet at δ 5.44 (1 H), olefin resonances which indicated the presence of an exocyclic methylene group, and a trisubstituted double bond. The other four GC peaks each showed only single olefinic resonances in the δ 5.5 region and thus were assigned the fused–fused structures **21a,b** and **22a,b** (R = H). So far, we have not found either of the bridged–bridged dimers **18** or **19** (R = H), although a bridged–bridged dimer **18** or **19** (R = Me) is a prominent product from the dimerization of the isopropylidene diyl **1**.[4c,16]

Photolysis of diazene **5** in the same solvents at 0° gave a mixture of dimers whose composition was essentially the same as that of the mixture obtained from pyrolysis.

A major goal of our work on TMM chemistry has been the elucidation of the role of the bicyclic hydrocarbon systems, 2-alkylidenebicyclo[2.1.0]pentane (**23**) and bicyclo[3.1.0]-hept-1-ene (**24**), which are the covalent tautomers of the 2-

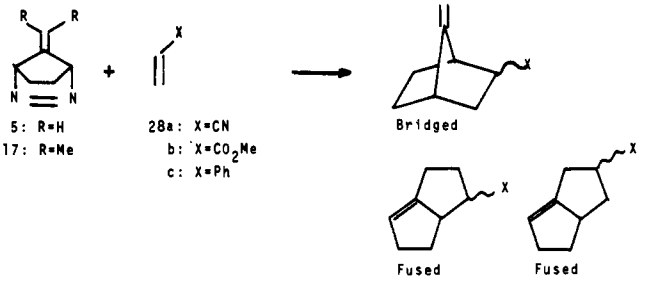


alkylidenecyclopenta-1,3-diyls. Recently, we have observed that hydrocarbons **23** (R = H or R = Me) give the same dimers as are obtained in the thermolysis of the corresponding diazenes **5** or **17**. The dimerizations of **23** undoubtedly occur by a preliminary cleavage of the bridge bond to form the diyl **4** or **1**.[17] However, hydrocarbons **24a**[19] and **24b**[20,21] of the bicyclo[3.1.0]hex-1-ene series dimerize in a different manner. Compound **24a** dimerizes spontaneously when generated at −90°C, even in dilute solution, to give three products, **25a–27a**,



with intact cyclopropane rings. By analogy, if the diyl **4** were capable of cyclizing to the corresponding bicyclo[3.1.0]hex-1-ene (**28**), dimers **25b** and **27b** might be expected in the product mixture. The cyclopropyl methylene ^{1}H and ^{13}C

Scheme V



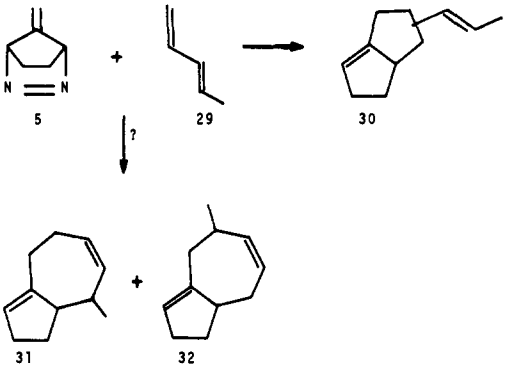
NMR resonances should provide a strong indication of the presence of such products, since they occur at higher field than any of the resonances expected for TMM dimers **18–22**.[19] For example, dimer **25a** has a proton resonance at δ 0.59, and dimer **27a** has two high-field resonances at δ 0.50 and 0.24. Similarly, **25a** and **27a** both show ^{13}C resonances near 11.6 ppm.[19] However, the dimer mixture from diazene **5** showed no proton resonances above δ 0.9 and no ^{13}C resonances above 23 ppm. It seems unlikely that substantial amounts of bicyclo[3.1.0]hex-1-ene dimers can be present in the product from diazene **5**.

Cycloadducts with Substituted Olefins. To establish that the 7-methylenecyclopenta-1,3-diyl singlet **4** shows the same preference for fused cycloadduct formation observed[4] in the reactions of the 7-isopropylidene analogue **1**, we have carried out thermal decompositions of diazene **5** in the neat olefins acrylonitrile (**28a**), methyl acrylate (**28b**), and styrene (**28c**). The olefin concentration was kept as high as possible to achieve the maximum proportion of product by the singlet route.[4] From each of these monosubstituted olefins, two bridged and four fused products may be formed (Scheme V).

Acrylonitrile gave four products, all of which were fused, since the vinyl-proton region of the NMR spectrum showed a resonance of unit intensity near δ 5.4. No absorptions were observed near δ 4.8, where the exocyclic methylene protons of the bridged adducts should have appeared. By the same criteria, methyl acrylate also gave only the four fused adducts. With styrene, the major products again were fused, although the two bridged adducts were observed to be formed in a combined yield of about 6%.

Cycloadducts with Conjugated Dienes. The proposed test of theory outlined in Table III reduces to the question whether there is a switch in regioselectivity between 1,2 and 1,4 addition to a conjugated diene. Ideally, this test would be most convincing if the orientation in the two modes of addition could be observed in a single diene, where differences in steric factors extraneous to the test might be minimized.

Our initial attempts to construct such a test involved additions to the piperylenes. With *trans*-piperylene (**29**), a major



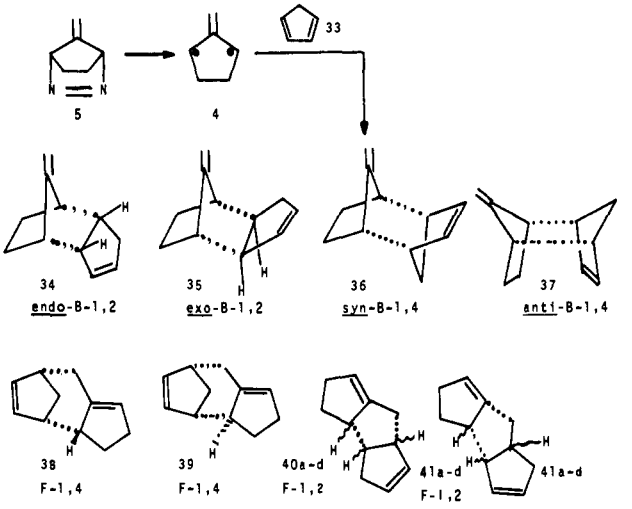
product was the fused 1,2 adduct **30**. The NMR spectra of the adduct mixtures could not be used readily to determine whether fused 1,4 products **31** or **32** were present. Similar results were obtained with *cis*-piperylene.

Table IV. Identifications of Some of the Cycloadducts of Diyl **4** and Cyclopentadiene

	structure and sobriquet	emergent position in GC	indep synth?	identified in product mixture?
34	*endo*-B-1,2	1	yes	yes
35	*exo*-B01,2		yes	no[a]
36	*syn*-B-1,4	3	yes	yes
37	*anti*-B-1,4	4	no	yes
38	*endo*-F-1,4		yes	no[a]
39	*exo*-F-1,4		yes	no[a]
40	F-1,2	2, 5-7	no	yes[b]
41	F-12		no	yes[b]

[a] A component of ⩾1% could have been detected. [b] Four isomers of F-1,2 were observed.

Scheme VI. Possible Cycloadducts of Cyclopentadiene and Diyl 4[a]



[a] The dotted lines represent the interannular bonds formed in the cycloaddition.

Ultimately, we reasoned that the use of acyclic dienes in the proposed test might be inadvisable because the desired concerted 1,4 cycloaddition would require the s-cis diene conformation rather than the thermodynamically favored s-trans form. A better chance for 1,4 addition could be provided by a cyclic diene in which the s-cis conformation was ensured by tying the 1 and 4 carbons together in a ring. For this reason, we turned to cyclopentadiene as the trapping agent.

Cyclopentadiene (**33**) is capable of forming 14 different cycloadducts with the TMM **4.** These are summarized in Scheme VI. From the reaction mixture obtained upon pyrolysis of diazene **5** in neat cyclopentadiene, we have isolated and identified seven of these adducts. In some instances the structures were established by independent synthesis. Moreover, the absence of three of the possible adducts was confirmed by independent synthesis of the missing isomers and demonstration that GC peaks and NMR absorptions of the authentic materials were not observed in the product mixture.

Table IV lists the substances whose presence or absence was established. Descriptions of the detailed proofs of structure are given in the following paragraphs, but the general reader may resume the mechanistic arguments in the section headed "Regiochemistry and Stereochemistry of the Cycloaddition of Singlet Diyl **4**".

Bridged 1,2 Adducts 34 and 35. Repeated preparative gas chromatography of the reaction mixture yielded five adduct fractions which were homogeneous by GC and NMR and two enriched adduct fractions, in addition to cyclopentadiene dimer and diyl dimers **18–22.** All of the adducts showed the correct elemental analysis and parent peak (*m/e* 146) in the mass spectrum. The NMR absorptions and structural assignments are listed in Table V.

The first emergent adduct was identified as a bridged 1,2 species by the characteristic high-field olefinic singlet absorption at δ 4.6 (2 H, $=CH_2$) and two one-proton olefinic multiplets centered at δ 5.77 and 5.45. The near identity in chemical shifts of the two exocyclic methylene protons suggested that the cyclopentene double bond was too far away to effect any differential shielding and led us to a tentative assignment of the endo configuration **34** to this adduct. This assignment was verified by two convergent authentic syntheses of the adduct from the known[22] *endo*-cyclopentadienone dimer **42** (Scheme VII). The NMR spectrum and GC retention time of the product **34** so obtained were identical with those of the first-emergent GC fraction from the cycloaddition.

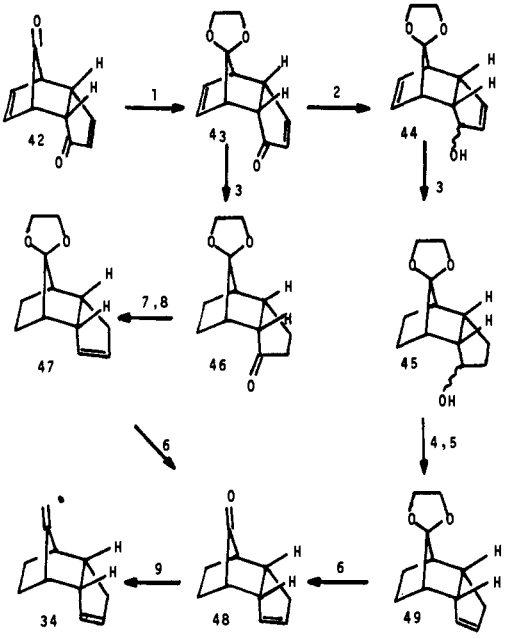
The exo isomer **35** was prepared from the ketone **50,** which was a minor product of the reaction of *trans*-2,5-dibromocyclopentanone (**51**) with diiron nonacarbonyl and cyclopenta-

Table V. NMR Spectral Data for the Adducts Obtained from Diazene **5** and Cyclopentadiene

order of elution[a]	isomer[a]	vinyl	allylic	bridgehead	$-CH_2-$
1	*endo*-B-1,2 **34**	5.77 (m, 1 H)	3.082 (m, 1 H)		1.4 (m, 4 H)
		5.45 (m, 1 H)			
		4.59 (s, 2 H)	2.2–2.6 (m, 5 H)[b]		
2	F-1,2[c]	6.01 (m, 1 H)			
		5.96 (m, 1 H)			
		5.08 (m, 1 H)			
3	*exo*-B-1,4 **36**	5.82 (s, 2 H)		2.45 (m, 2 H)	1.75 (d, 1 H)
		4.18 (s, 2 H)		2.22 (m, 2 H)	1.49–1.69 (m, 4 H)
					1.20 (d of t, 1 H)
4	*endo*-B-1,4[c] **37**	6.28 (s, 2 H)			
		4.48 (s, 2 H)			
5	F-1,2 **40** or **41**	5.72 (m, 1 H)	2.5–2.61 (m, 6 H)	2.90 (m, 1 H)	2.23 (m, 1 H)
		5.60 (m, 1 H)	2.23 (m, 1 H)		1.79 (m, 1 H)
		5.25 (bs, 1 H)			1.47 (m, 1 H)
6	F-1,2 **40** or **41**	5.65 (m, 1 H)	1.25—2.52 (m,	3.48 (m, 1 H)	
		5.60 (m, 1 H)	10 H)[b]		
		5.21 (bs, 1 H)			
7	F-1,2 **40** or **41**	5.67 (m, 1 H)	2.2–2.7 (m, 6 H)	3.44 (m, 1 H)	2.0 (m, 2 H)
		5.57 (m, 1 H)		3.16 (m, 1 H)	1.55 (m, 1 H)
		5.25 (bs, 1 H)			

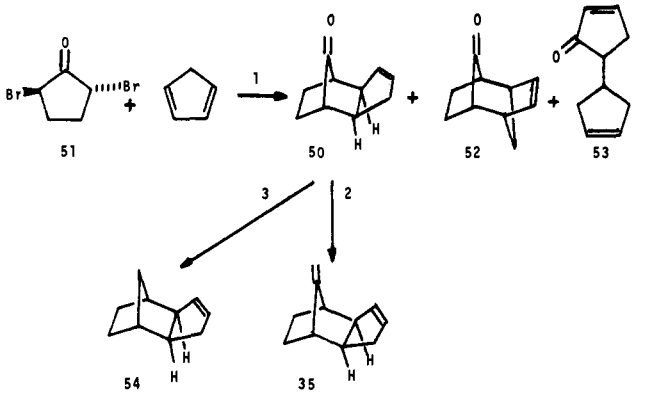
[a] Adducts appear in the order in which they emerge from the GC column. [b] Also includes the aliphatic protons. [c] Sample not pure enough to assign remaining resonances.

Scheme VII. Syntheses of the *endo*-B-1,2 Adduct **34**



1. $HOCH_2CH_2OH$, TsOH; 2. $NaBH_4$, MeOH; 3. H_2, Pd/C; 4. $SOCl_2$, pyr; 5. *t*-BuOK, Me_2SO; 6. 5% H_2SO_4; 7. $TsNHNH_2$, MeOH; 8. MeLi, Et_2O; 9. $Ph_3P{=}CH_2$.

Scheme VIII



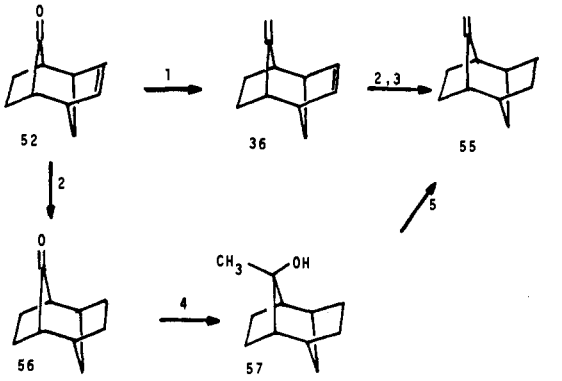
1. $Fe(CO)_9$, PhH; 2. NaH, Me_2SO, Ph_3PCH_3I; 3. H_2NNH_2, KOH diethylene glycol.

diene (Scheme VIII). Presumably, this reaction involved the five-membered analogue of the six- and seven-membered ring complexed species previously employed by Noyori and his co-workers to effect addition of an oxyallyl unit to a conjugated diene.[23,24] The major product was the [3 + 4] adduct **52**, which was used later in the synthesis of the bridged 1,4 adduct **36** (see Scheme IX).

The stereochemistry of ketone **50** was established by Wolff–Kishner reduction to the known[25] dihydro-*exo*-dicyclopentadiene **54**. Wittig methylenation of ketone **50** gave the *exo*-B-1,2 adduct **35**. The exocyclic methylene protons of **35** gave rise to separate resonances at δ 4.68 and 4.60, in contrast to the single chemical shift observed for the *endo*-B-1,2 isomer **34**. This was in accord with expectation that differential shielding should be more important in the exo isomer because the endocyclic double bond is close to the $=CH_2$ protons.

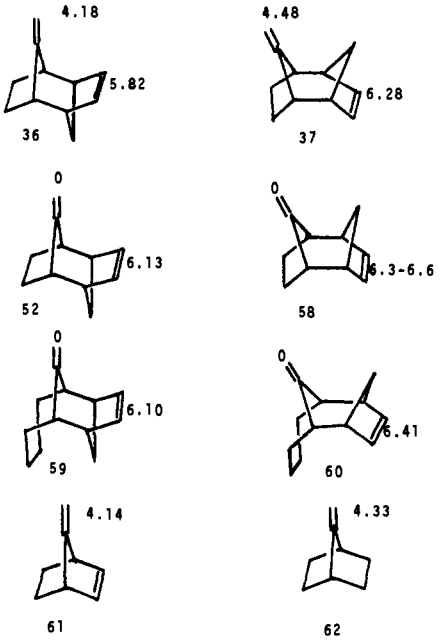
These proton absorptions constituted a clearly discernible analytical marker for the presence of *exo*-B-1,2 adduct **35** and facilitated a search of all the adduct fractions for its presence. We were unable to find these resonances in the cycloaddition product mixture from the diazene–cyclopentadiene reaction. If present, the *exo*-B-1,2 adduct probably did not account for more than 1% of the products.

Scheme IX



1. Ph_3PCH_3I, MeLi, Et_2O; 2. H_2, Pd/C; 3. sepn; 4. MeLi, Et_2O; 5. $SOCl_2$, pyr, 0°.

Scheme X. ^1H NMR Shifts (δ Units)

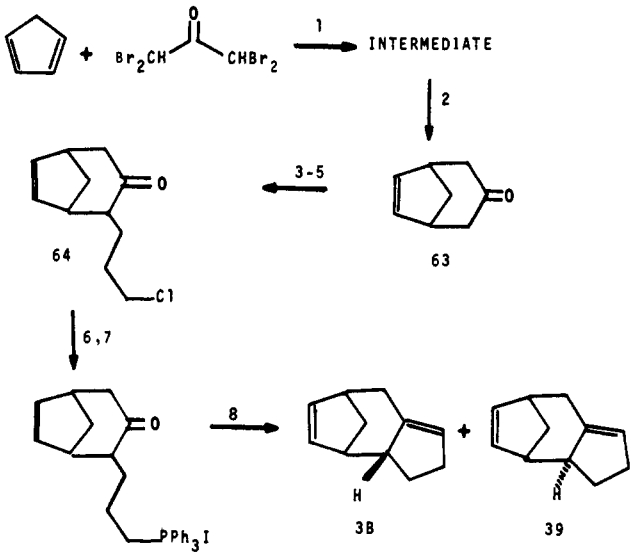


Bridged 1,4 Adducts 36 and 37. The third and fourth emergent peaks from the GC analysis contained the *syn*- and *anti*-B-1,4 adducts **36** and **37**. The syn compound **36** was independently synthesized (Scheme IX) by Wittig methylenation of the major component **52** (Scheme VIII) of the 2,5-dibromocyclopentanone–cyclopentadiene–iron tricarbonyl reaction. Although generation of the Wittig reagent by the sodium hydride–Me_2SO procdure[26] led to destruction of the starting ketone and gave no appreciable amount of the diene **36**, the use of methyllithium as the base and refluxing ether as the solvent gave a 50% yield of **36**. So prepared, the material was identical in all respects with the third emergent adduct (Scheme IX). Moreover, the dihydro derivative **55**, separated by GC from the mixture formed by partial hydrogenation of adduct **36**, was independently synthesized by the sequence shown in Scheme IX.

As Table V shows, the olefinic and bridgehead ^1H NMR absorptions of *syn*-B-1,4 adduct **36** occurred in pairs, as befitted the proposed twofold molecular symmetry. The ^{13}C NMR showed only seven lines, which confirmed the symmetrical structure. Double-resonance experiments supported the NMR assignments.

The stereochemical assignment depended upon the observed mutual shielding effects of the two unsaturated systems in the diene **36** and its precursor ketone **52**, which were analogous to those found for the model compounds **59–60**[27] and **61–62**[28] (Scheme X). The observed regularities justified the assign-

Scheme XI. Synthesis of the F-1,4 Adducts 38 and 39



1. $Fe(CO)_5$, THF/PhH; 2. Zn/Cu, NH_4Cl, MeOH; 3. cyclohexylamine, TsOH, PhH; 4. EtMgBr; 5. $Br(CH_2)_3Cl$; 6. NaI, acetone; 7. Ph_3P, PhH; 8. *n*-BuLi, THF.

ments of the syn (**36**) and anti (**37**) configurations, respectively, to the third and fourth emergent adducts (see Tables IV and V).

While this work was in progress, Ernst and Ganter[29] reported that a mixture of the symmetrical ketones **52** and **58** was formed when 5-chloro-1-morpholinocyclopentene and cyclopentadiene were condensed in the presence of a Lewis acid catalyst. Dr. Ganter has kindly provided ^1H and ^{13}C NMR spectra of these samples. Those of the syn isomer **52** exactly matched the spectra of our compound **52** obtained by the $Fe_2(CO)_9$-induced condensation of Scheme VIII.

It is noteworthy that we did not find appreciable quantities of the anti isomer **58** in the latter reaction. We do not know whether this is attributable to the absence of a kinetically achievable pathway or to a thermodynamic instability of **58** under the reaction conditions. In the latter connection, it may be significant that a minor component (~9%) of the condensation reaction mixture of Scheme VIII was an isomer of **52** and **58** whose ^1H NMR spectrum was consistent with the structure **53**. The origin of this material is not certain, but the possibility that it might be formed from the "missing" isomer **58** can be tested experimentally now that **58** has become available by the Ernst-Ganter[29] route.

Fused 1,2 Adducts 40 and 41. Each of the final three peaks to emerge from the GC separation of the products of the reaction of cyclopentadiene with diazene **5** contained a compound that showed two olefinic proton resonances at δ 5.6–5.7 and one-proton singlet at δ 5.2. These features and the empirical composition strongly suggested structure **40** or **41**. We did not attempt to define which three of the eight possible isomers of the **40–41** series our products were. Our tentative assignment of these compounds as fused 1,2 (**40, 41**) rather than fused 1,4 (**38** or **39**) was based upon the olefinic proton chemical shifts, which in all three instances occurred at substantially higher field than the endocyclic olefinic protons of model compounds (see Scheme X). Adherence to such analogies would have led us to expect the olefinic protons of the bridged ring of **38** or **39** to resonate below δ 6.

We have verified these assignments by independent syntheses of **38** and **39** according to the sequence outlined in Scheme XI. Formal conjugate cycloaddition of an unsubstituted oxyallyl fragment to cyclopentadiene was effected by the method of Noyori and co-workers.[30] The reaction of $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone and excess cyclopentadiene in the presence of iron pentacarbonyl followd by reduction of the intermediate with zinc–copper couple led to a 30% yield of pure, sublimed bicyclo[3.2.1]oct-6-en-3-one (**63**).[31]

Alkylation of this ketone with 1-bromo-3-chloropropane, using the conjugate base of the imine,[32] gave **64**, in which the side-chain stereochemistry is undefined. The subsequent steps shown in Scheme XI culminated in a smooth intramolecular Wittig cyclization which led to an approximately equimolar mixture of the two stereoisomeric tricyclic dienes, **38** and **39**. These compounds were separated by GC, and each had the required elemental composition and NMR spectroscopic properties.

The Experimental Section gives the details of the demonstration that neither of these dienes was present to the extent of $\geq 1\%$ in the product mixture from the capture of diyl **4** in neat cyclopentadiene or in a dilute solution of cyclopentadiene in acetonitrile.

We may summarize the qualitative results of the cycloaddition of thermally generated **4** and cyclopentadiene by reference to Table IV. Adducts *endo*-B-1,2, both *syn*- and *anti*-B-1,4, and four of the F-1,2 adducts constituted the bulk of the reaction mixture. The way now was clear to establish quantitatively the product composition characteristic of *singlet* diyl **4** and thereby address the question of regioselectivity.

Dilution Studies to Determine the Singlet Product Composition. Previous studies[4] had shown that the closely related TMM, 2-isopropylidenecyclopenta-1,3-diyl (**1**), when thermally generated, gave products whose distribution depended on the concentration of the trapping olefin. High olefin concentrations favored the formation of stereospecific and regiospecific addition products, but the composition of the products became more stereorandom and regiorandom as the olefin concentration decreased. This "dilution effect" was interpreted in terms of a cascade mechanism, in which an initially formed singlet species could be intercepted but, at low olefin concentration, eluded capture and crossed over to the ground-state triplet diyl. Also, the triplet diyl could be selectively scavenged by oxygen. Thus, in an oxygen-saturated system, it was possible to obtain the typical singlet product distribution even at low olefin concentration.[4]

However, these devices for achieving "pure singlet" behavior of the diyl **4** in its reactions with cyclopentadiene proved to be of limited value. Attempted oxygen saturation experiments were unsatisfactory because of the rapid autoxidation of cyclopentadiene. We did observe pronounced effects on the product composition upon dilution (see Figure 1), which left no doubt that the limiting singlet product, formed at the highest cyclopentadiene concentration, was composed largely of F-1,2 and B-1,4 adducts, but the quantitative analysis of the products was difficult because the dicyclopentadiene formed in large quantities by dimerization of cyclopentadiene obscured the GC region where the adduct peaks emerged. Moreover, this dimerization of cyclopentadiene itself caused an inevitable change in the concentration of the trapping olefin. Since dicyclopentadiene, like other nonconjugated olefins,[3] is not an efficient diylophile, it would act as an inert diluent, causing a gradual decrease in the diene concentration during a run.

To circumvent these difficulties, we turned to a photochemical method for generation of the diyl **4**. Previous studies[4e] had shown that the direct photodeazetation of diazene **17**, the precursor of the TMM 2-isopropylidenecyclopenta-1,3-diyl (**1**), generated a species which, aside from a temperature effect, behaved like the thermally produced singlet. In particular, the photolytic system showed the typical dilution effect on the product composition.

Photolysis of diazene **5** in neat cyclopentadiene gave a mixture of cycloadducts similar to that obtained in the thermal deazetation experiments. A control experiment showed that the photolytic reaction conditions sufficed to decompose the

Table VI. Products from the Photolysis of Diazene **5** in Neat Cyclopentadiene at 0 °C

order of emergence[a]	structural assignment	% yield[b]
1	F-1,2α (**40–41**)	0.5
2	*exo*-B-1,2 (**35**)	<2.5[c]
3	*endo*-B-1,2 (**34**)	1.0
4	*syn*-B-1,4 (**36**)	34.0
5	*anti*-B-1,4 (**37**)	2.0
6	F-1,2β (**40–41**)	
7	F-1,2γ (**40–41**)	17.0[d]
8	F-1,2δ (**40–41**)	42.0

[a] GC column OV-17 at 80 °C. [b] Relative yield. The absolute material balance was 97%. [c] This fraction contained **35** and at least one other component. [d] Fractions 6 and 7 were not well separated by the GC column. The yield is the sum of the two components.

starting diazene, so that none of the products was formed by thermal decomposition of unreacted diazene in the GC injector port. The GC analyses of the photolytic products benefited from the use of an OV-17 column, which proved more efficient than the γ-nitro-γ-methylpimelonitrile column used in the analysis of the thermal product mixtures.

Table VI lists the eight products identified in the photolysis reaction mixture. Products **3–8** were shown by GC coinjection studies and ^{1}H NMR spectroscopy of isolated fractions to be the *endo*-B-1,2 adduct **34** (see Scheme VI for structures), the *syn*- and *anti*-B-1,4 adducts **36** and **37**, and three of the F-1,2 series **40** and **41** (F-1,2β,γ,δ). In addition, the chromatograms showed two peaks cleanly separated from the dicyclopentadiene peak which constituted about 3% of the total adduct mixture. GC–mass spectral analysis of these fractions showed the expected cycloadduct parent peak (*m/e* 146) to be present. The first emergent of these two adducts constituted only 0.5% of the adducts. It was not isolated, but, since all of the other structures had been identified with other peaks, this peak, by exclusion, was assumed to be a F-1,2 isomer (F-1,2α). The second peak (2.5%) was shown by NMR to contain two components. Two protons of one of the components had the same chemical shifts previously observed for the exocyclic methylene protons (δ 4.68 and 4.60) of the *exo*-B-1,2 adducts **35**. Coinjection of authentic independently synthesized **35** with the gas chromatographically enriched sample of the "second peak" confirmed the assignment. We therefore could place an upper limit of 2.5% of **35** in the photolytically generated adduct mixture.

The authentic F-1,4 adducts **38** and **39**, synthesized as previously described (Scheme XI), had the same retention time (by coinjection) as the *syn*-B-1,4 adduct **36**. However, the ^{1}H NMR spectrum of an enriched sample with this retention time isolated from the cyclopentadiene + **5** reaction mixture showed only the signals of *syn*-B-1,4 adduct **36** under conditions where 3% of either of the F-1,4 adducts could have been detected. Since the *syn*-B-1,4 adduct constituted 34% of the adduct mixture, we may conclude that neither of the F-1,4 products **38** and **39** comprises more that 1% of the adducts.

Figure 2 shows the effect of concentration on the composition of the adducts. There was a sharp increase in the percentage of both *syn*-B-1,4 and F-1,2-δ with concentration of the trapping agent. Since the diyl **4** has a triplet ground state,[11b] singlet **4** would have been expected to decay to the triplet unless it were intercepted before intersystem crossing could occur. The observed concentration effect thus strongly suggested that *syn*-B-1,4 and F-1,2δ were singlet derived.

Conversely, products *exo*-B-1,2 and *anti*-B-1,4 both increased upon dilution and hence were formed, at least in part, by capture of the triplet daughter diyl. Although Figure 2 plots F-1,2β and γ as one component, it was clear from the GC

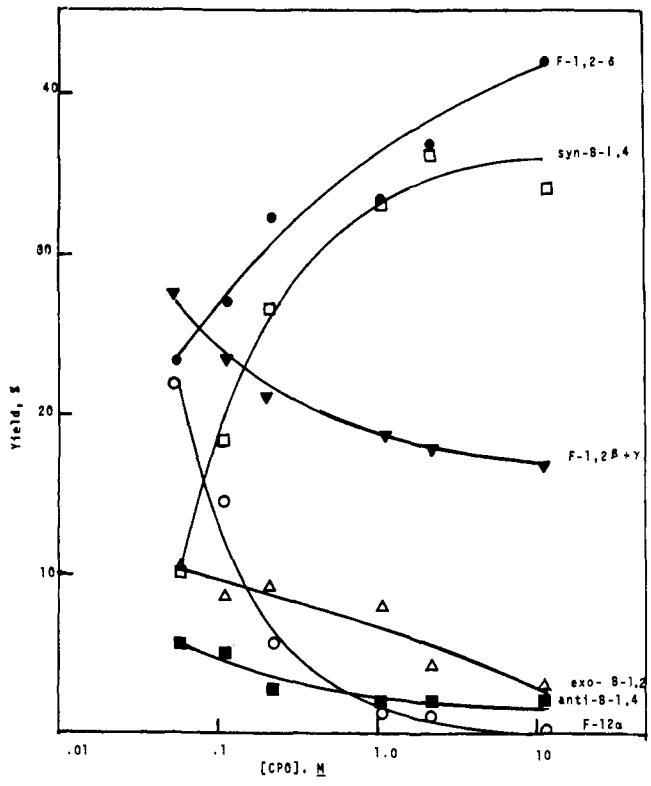


Figure 2. Product composition as a function of concentration of cyclopentadiene [CPD] in the photolysis of diazene **5** in CH_3CN. The data for two minor products, peaks 1 and 3 of Table VI, are not shown. The highest concentration points refer to reactions in neat cyclopentadiene.

traces that the yield of F-1,2γ remained roughly constant with dilution, whereas that of F-1,2β increased.

Adduct F-1,2α also increased dramatically with dilution. We conclude that F-1,2α and -β are formed largely from triplet diyl at low [CPD].

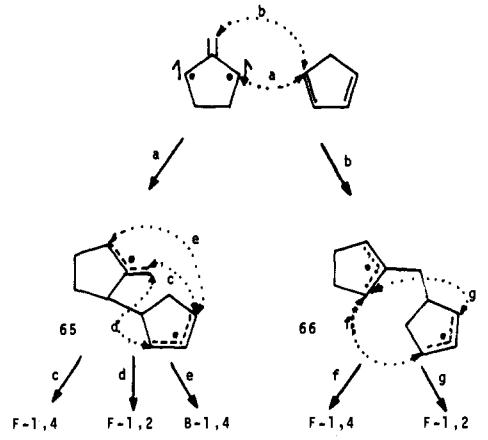
Discussion

If we use the composition of the products obtained from the photolysis in neat cyclopentadiene (Table VI) as the closest feasible approach to the limiting distribution from the pure singlet diyl, we may describe the results as representing almost entirely (>95%) two types of adducts, B-1,4 and F-1,2. Minor amounts (~3%) of B-1,2 adducts and little if any (<1%) of F-1,4 adducts were observed. If the ordering of the diyl nominal NBMOs was S below A, these results would be in full accord with the predictions of the orbital-symmetry model (Table III).

In the bridged series, the "allowed" products *syn*-B-1,4 (**36**) and *anti*-B-1,4 (**37**) predominated over the "forbidden" ones *exo*-B-1,2 (**35**) and *endo*-B-1,2 (**34**) by a ratio of 10:1. This was a minimum value, because the percentage of the "forbidden" product *exo*-B-1,2 given in Table VI was an upper limit. Moreover, since dilution decreased the "allowed":"forbidden" ratio in the bridged series (Figure 2), we could not be sure, even using a neat cyclopentadiene medium, that we really eliminated reaction of the triplet diyl and intercepted only the singlet. Of the two "allowed" bridged adducts, the *syn*-B-1,4 product **36** predominated over its anti stereoisomer **37** by a ratio of about 17:1, again qualitatively in accord with the prediction based upon a symmetric HOMO for the singlet diyl. Note (Figure 2) that the syn:anti ratio of the B-1,4 products approached unity in very dilute solution, where the product was largely of triplet provenance and the frontier orbital predictions of Table III did not apply.

In the fused series, the results again indicated high regioselectivity in the singlet addition. None of the "forbidden"

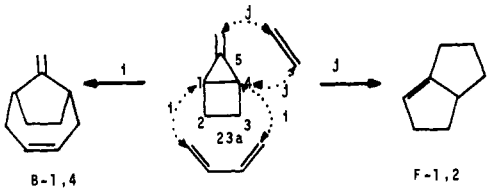
Scheme XII. Triplet Cycloaddition



F-1,4 products was observed, so that the "allowed":"forbidden" ratio could be given as at least 100:1. It was not clear that all of this selectivity was attributable to orbital symmetry factors in the singlet addition, since F-1,4 did not seem to be formed in appreciable amounts even in dilute solutions, where triplet-derived products were significant. We can only speculate on the reasons why triplet diyl **4** gave little if any F-1,4 product, but it seems significant that the triplet diyl did not form any of the other singly or doubly bridged products *endo*- and *exo*-B-1,2 (**34** and **35**) or *syn*- and *anti*-B-1,4 (**36** and **37**) in large amounts either. At the lowest concentration studied (0.055 M cyclopentadiene), 81% of the adduct mixture consisted of F-1,2 products. The addition of triplet diyl is a stepwise process, so that the first bond may be formed either at a ring site or at the exocyclic methylene position. The intermediates, **65** and **66**, respectively, each may cyclize by competing paths, one of which leads to a F-1,2 adduct and the others to adduct(s) containing one or two bridges. It would not be surprising if the strain in the latter products retarded their formation in this second step (Scheme XII, c, e, f. The path to B-1,2 is not shown).

Without modification, the bisected singlet hypothesis fails to account for the switch in regioselectivity between 1,2 and 1,4 cycloaddition (Table III). We recognize the possibility that *both* a planar and a bisected diyl may be involved in the singlet cycloaddition. One then might construct a mechanism in which the bisected singlet is the precursor of the F-1,2 product and the planar singlet leads to the B-1,4 product. This hypothesis cannot be excluded on the basis of the present data, but it is certainly less economical and therefore, at present, less useful than the orbital symmetry rationale.

One subtle problem remains in our attempt to identify the reactive form of the singlet species. The attentive reader will perceive that, if the reactive singlet were not the the true diyl **4** but instead its bicyclic valency tautomer **23a**, a set of orbital symmetry predictions identical with those of Table III would ensue. Thus, the formation of B-1,4 and F-1,2 adducts would



correspond to $[{}_{\sigma}2_s + {}_{\pi}2_s + {}_{\pi}2_s]$ "allowed" [4 + 2] reactions in which the bridge σ bond of **23a** acts as a dienophilic two-electron component in the first instance (i) and as a part of the four-electron "diene" component in the second (j). In other words, the bond orbitals at the bridgehead positions (C-1 and C-4) of the bicyclic hydrocarbon **23a** are necessarily *in phase* because those centers are bonded. This makes them equivalent in their qualitative orbital symmetry function to the S-HOMO of diyl **4**.

Compound **23a** has recently been prepared.[17] It is thermally unstable in solution at temperatures above −65 °C, giving the characteristic dimers (Scheme IV) of the triplet diyl. At 0 °C, the temperature of our photolyses, the lifetime of **23a** therefore cannot be greater than a fraction of a second, and under our conditions we have whatever mixture of **23a** and singlet diyl **4** the various rate constants of the system permit. Compound **23a** is thus an *available* candidate for cycloaddition.

In principle, kinetic methods exist for making the subtle distinction between **23a** and diyl **4** as the actual reactive species. We hope soon to report the results of some experiments along this line, but we note already that a *general* explanation of singlet TMM behavior in terms of the bicyclic tautomer as the reactive entity cannot be correct, since it predicts products in conflict with experiment in the case of bismethoxymethylenecyclopenta-1,3-diyl described elsewhere.[1,33] For the present, the planar diyl with appropriate HOMO phase properties provides the only unifying hypothesis of TMM singlet reactivity. We recognize that future events may necessitate a sacrifice of hypothetical simplicity for actual complexity.

We also emphasize that, even if the planar diyl should prove to be the reactive species, no direct information thereby would be provided on the energy ranking of the planar diyl, the bisected diyl, and the bicyclic form. All that the present hypothesis requires is that the planar species be energetically accessible under the reaction conditions.

When we look beyond our phenomenological correlation for a justification of the S-below-A ordering of the NBMOs of the singlet diyl **4**, we find the theoretical approaches to the problem still at an early stage of development. Although it is qualitatively true that the contraction of the endocyclic TMM bond angle in **4** tends to stabilize the S component because of the in-phase transannular interaction,[34a] more detailed calculations at the STO-3G-CI level[34b] suggest that this effect would be small. In unsubstituted TMM, contraction of the C-2–C-4–C-3 angle from 120 to 110° causes a splitting of only 0.2 kcal/mol. More recently, HMO (EH) calculations[34c] on 2-methylenecyclopenta-1,3-diyl (**4**), although they agree with the STO-3G-CI results in predicting that the angular contraction effect would be small, also predict a large splitting (18 kcal/mol) by the interaction of the TMM π orbitals with the σ orbitals of the bridging CH_2 groups in the ring. This is predicted[34c] to selectively destabilize the A component and thus would provide a theoretical rational for our observations. It would be useful to know whether so large a splitting would survive a more sophisticated calculation.

Finally, we must emphasize that the frontier MO rationalization of the regioselectivity in the reactions of the singlet diyl **4** implicitly disregards a major difference between the MO properties of biradicals and conventional stable molecules. In an ordinary molecule, the ground-state HOMO–LUMO separation is large, and it is a basic assumption of the simple form of frontier MO theory[8] that the energetic ordering and charge-density distributions of each partner's HOMO and LUMO offer a reliable guide to the corresponding properties in the cycloaddition transition state. In a biradical, however, the HOMO–LUMO separation often is small. Consequently, the presence of the cycloaddition partner molecule in the transition state could conceivably perturb the electron distribution so strongly that the forbidden transition-state orientation (that is, the one with out-of-phase frontier orbital overlaps between the partners) becomes more stable. The regioselectivity of the reaction then would not be "frontier-orbital controlled" and would offer no direct evidence on the phase properties of the HOMO and LUMO of the diyl. It seems clear that the next stage of theoretical development of the cycload-

dition reactions of biradicals should go beyond the crude frontier MO theory and begin to investigate directly the energy characteristics of the competing approach pathways.

Experimental Section

Instruments. Routine nuclear magnetic resonance (NMR) spectra were taken on a Varian A-60A or a Perkin-Elmer R-32-90 spectrometer in deuteriochloroform or carbon tetrachloride. Chemical shifts were measured relative to tetramethylsilane (Me_4Si) and are recorded as follows: chemical shift (parts per million downfield from Me_4Si), multiplicity, number of protons, coupling constants (when measured), and assignment. High-quality ^1H NMR spectra were obtained on a Bruker HX 270 instrument.

^{13}C NMR spectra were also obtained on a Bruker HX 270 instrument. Chloroform-*d* was used as solvent and as the lock compound. Chemical shifts are given in parts per million downfield from Me_4Si, and the coupling constants, when noted, are in parts per million and/or hertz. In off-resonance decoupled ^{13}C spectra, the multiplicities are also given.

Infrared (IR) spectra were recorded on Perkin-Elmer Model 237 or Beckman IR 4250 spectrophotometers, usually in carbon tetrachloride. All spectra were calibrated with reference to 1601.4-cm^{-1} polystyrene absorption band.

Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6 single-focusing instrument. High-resolution mass spectra were taken by Dr. Walter McMurray and Mr. Craig Whitehouse of the Division of Health/Physical Sciences at Yale University.

Preparative gas chromatography (GC) was performed on a Varian Aerograph 90-P-3 with helium as the carrier gas, using columns as indicated. For analytical GC, a Perkin-Elmer 900 gas chromatograph equipped with nitrogen carrier gas and a flame ionization detector was used. Usually, 0.125-in. packed columns were utilized for any analytical studies. GC peak integrals were recorded using a Hewlett-Packard 3700A digital integrator. In cases of severely drifting base line or nonresolved peaks, an assumed base line was sketched and a Xerox copy of the chromatogram was cut out and weighed. Usually five such weighings were done for each questionable peak.

Small quantities of material were measured volumetrically with either a 10-, 50-, 100-, or 250-μL Hamiltion syringe. When the smallest of these was used for injection of a sample onto the analytical VPC, the following technique was necessary for reproducibility. About 1 μL of solvent was drawn up, followed by about 0.5 μL of air and then the sample of interest. This assures injection of the complete sample onto the column and prevents the irreproducible results caused by the fractional volatization of material remaining in the needle in the injection port.

Reagents. Chemicals used were reagent grade or better. Solvents used for the azo decompositions were spectral grade and were dried with molecular sieves. Other solvents were not dried or distilled before use unless noted.

Standard procedures for the preparation of pyrolysis and photolysis samples and for GC analyses have been described elsewhere.[4c]

Pyrolyses were run in a heated, 2-L beaker filled with oil and constantly stirred to maintain the bath temperature at 60 ± 3 °C. Photolyses were run in a Rayonet reactor (Southern New England Ultraviolet Co.) containing 16 350-nm lamps unless otherwise noted. The sample tubes were placed in a beaker which was fitted inside of an unsilvered Dewar cylinder. The tubes and the beaker were surrounded by an ice/water bath. Photolyses were usually run for 8 h (unless noted otherwise).

Synthesis of 7-Methylene-2,3-diazabicyclo[2.2.1]hept-2-ene (5) (Method A, Scheme II). Diethyl 7-Bromo-7-bromomethyl-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (11). To a precooled (0 °C, ice-acetone) flask containing 47.01 g (0.135 mol) of the bromo aldehyde **10**[14] dissolved in 600 mL of absolute ethanol was added dropwise over 15 min 2.53 g (0.0673 mol) of sodium borohydride in 200 mL of absolute ethanol. After stirring for 1 h at room temperature, the solution was washed with brine and extracted with chloroform. The organic layers were dried over $MgSO_4$ and removed in vacuo to give 44.5 g (97%) of a dark red-brown oil. IR (CCl_4); 3480, 2975, 2940, 1750, 1720, 1310, 1150, 995, 570, 460, 440 cm^{-1}. NMR: δ 4.5 (b, 2 H, bridgeheads), 4.25 (q, 4 H, carboethoxy methylene), 3.95 (s, 2 H, CH_2OH), 2.70 (bs, 1 H, OH), 1.95 (bs, 4 H, ring methylenes), 1.4 (t, 6 H, carboethoxy methyls). Mass spectrum: *m/e* 352 (P + 1) 350 (P − 1), 243, 184, 120, 118, 110, 82.

Under nitrogen, phosphorus tribromide (4.17 mL, 0.044 mol) and dry pyridine (1.3 g, 0.016 mol) were syringed into a precooled (0°C, ice bath) 1000-mL round-bottom flask containing 100 mL of dry benzene (distilled from sodium). To this stirred mixture at 0°C was added dropwise, over 3 h, a solution of 44.5 g (0.127 mol) of the bromohydrin obtained in the previous step in 200 mL of dry benzene, to which 1.2 g (0.015 mol) of pyridine had been added (total pyridine 2.5 g (0.031 mol)). The reaction mixture was stirred in the dark for an additional 72 h. The mixture was then washed with 10% HCl, methylene chloride was added, and the organic layer was separated and washed with 5% sodium bicarbonate solution. The combined organic layers were dried over $MgSO_4$ and doncentrated to give 36.75 g (70%) of a dark red material. IR (film): 3020, 2960, 1750, 1720, 1340, 990, 970, 570, 460, 440 cm^{-1}. NMR: δ 4.5 (bs, 2 H, bridgehead), 4.25 (q, 4 H, carboethoxy methylenes), 3.88 (s, 2 H, CH_2Br), 2.00 (bs, 4 H, ring methylenes), 1.4 (t, 6 H, carboethoxy methyls). Mass spectrum: *m/e* 418 (P + 4), 416 (P + 2), 414 (parent), 280, 198, 120; 118, 116, 85, 83.

If the reaction did not go to completion, the mixture was taken on through the next step, and bromohydrin was recovered from the column by rinsing with methanol.

Diethyl 7-Methylene-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (12). To 8.16 g (19.7 mmol) of the crude dibromide **11** dissolved in 160 mL of dry tetrahydrofuran (THF) were added 3.0 g (0.04 mol) of zinc-copper couple[39] and 1.66 mL of glacial acetic acid. The reaction mixture was refluxed overnight. The dark brown solution was filtered through a sintered funnel to remove the excess zinc and zinc bromide, and the filtrate was taken up in brine and extracted with ether. The ether layers were washed with 5% sodium bicarbonate solution and dried over $MgSO_4$. Removal of solvent in vacuo gave a yellow oil which could be further purified by percolation through 100 g of Florisil with 10% pentane/90% ether. Pure carbamate could be obtained in this manner with yields ranging from 85 to 95%. NMR: δ 4.97 (s, 2 H, terminal methylene), 4.58 (bs, 2 H, bridgeheads), 4.25 (q, 4 H, carboethoxy methylenes), 1.9 (bs, 4 H, ring methylenes), 1.4 (t, 6 H, carboethoxy methyls).

Mass spectral and elemental analysis of the corresponding dimethyl ester yielded mass spectrum *m/e* 226 (parent), 198, 154, 139, 127, 113, 112, 98, 95 (base), 80, 79, 77, 68, 59, 54, 42. Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.08; H, 6.23; N, 12.38. Found: C, 53.32; H, 6.08; N, 12.52.

7-Methylene-2,3-diazabicyclo[2.2.1]heptane (5). The methylene carbamate **12** (1.05 g, 4.64 mmol) was dissolved in ca. 3 mL of ether and added to 15 mL of degassed water. Potassium hydroxide (1.56 g, 27.84 mmol) was added and the solution heated to 85 °C and stirred under nitrogen overnight. The reaction mixture was then cooled and 6 N HCl was added cautiously (foaming) until pH 1. Potassium carbonate was added until pH 8, and the solution was extracted with degassed chloroform. To the chloroform solution in a separatory funnel was added 100 mL of cupric chloride solution. The mixture was shaken vigorously, and the water layer separated from the chloroform

Table VII. GC Columns Used

A	5 ft by 1/8 in. 20% CW-20M on 80–100 mesh Chromosorb P
B	5 ft by 1/4 in. 20% SE-30 on 60–80 mesh Chromosorb W
C	10 ft by 1/8 in. 1% CW-20M on 80–100 mesh Chromosorb P
D	12 ft by 1/8 in. 20% γ-methyl-γ-nitropimelonitrile on 80–100 mesh Chromosorb P NAW
E	10 ft by 3/8 in. 20% γ-methyl-γ-nitropimelonitrile on 60–80 Chromosorb P NAW
F	5 ft by 1/4 in. 20% γ-methyl-γ-nitropimelonitrile on 60–80 mesh Chromosorb P NAW
G	12 ft by 1/8 in. 25% γ-methyl-γ-nitropimelonitrile on 80–100 mesh Chromosorb P DMCS, AW
H	5 ft by 1/8 in. 5% DEGS on 100–120 mesh Chromosorb P DMCS, AW
I	5 ft by 1/4 in. 25% CW-20M on 60–80 mesh Chromosorb P
J	5 ft by 1/4 in. 10% DEGS on 60–80 mesh Chromosorb P
K	10 ft by 1/4 in. 25% β,β-oxydipropionitrile on 60–80 mesh Chromosorb P
L	10 ft by 1/4 in. 25% CW-20M on 60–80 mesh Chromosorb P
M	15 ft by 1/8 in. 1.5% TCEP on 100–120 mesh Chromosorb P
N	5 ft by 1/4 in. 5% CW-20M on 80–100 mesh Chromosorb P, DMCS, AW
O	20 ft by 1/8 in. 3% OV-17 on 80–100 mesh Anakrom ABS
P	5 ft by 1/4 in. 3% OV-17 on 60–80 mesh Anakrom ABS

layer without precipitation of the copper complex of the azo compound (water layer turned green or brown). After the water was extracted twice more with chloroform, the combined organic fractions were shaken with concentrated ammonium hydroxide until the water layer was colorless, dried over $MgSO_4$, and removed on the rotary evaporator until about 10 mL of solvent remained. Anhydrous potassium carbonate was added and solutions of azo compound prepared in this manner were indefinitely stable at −20 °C. Because of the instability and volatility of the azo compound, best results were obtained when all of the chloroform was not removed. NMR:[11] δ 5.15 (s, 2 H, bridgeheads), 4.78 (s, 2 H, terminal methylene), 1.1–1.9 (m, 4 H, ring methylenes).

Pure azo compound **5** could be obtained as low-melting, white crystals by passage through 20 g of Florisil with 20% ether/80% pentane. The material which eluted first was the azo compound. By flushing the column with ether, any starting carbamate **12** could also be recovered. Typical yields of azo compound from carbamate were 80–85%.

This entire sequence of reactions starting from 6-acetoxyfulvene was also carried out by using dimethyl instead of diethyl azodicarboxylate. All of the products and spectral data are consistent with the assigned structures.

(Method B, Scheme III). Dimethyl 7-(Dichloromethylene)-2,3-diazabicyclo[2.2.1]-5-heptane-2,3-dicarboxylate (15[35]). A 250-mL three-neck round-bottom flask, equipped with a mechanical stirrer, addition funnel, and nitrogen inlet, was charged with nickelocene (Aldrich) (5.0 g, 0.027 mol), triphenylphosphine (7.0 g, 0.027 mol), and 100 mL of dry ether. A solution of carbon tetrachloride (4.15 g, 0.027 mol) in 50 mL of ether was added dropwise to the stirred suspension. The reaction mixture was stirred for an additional 17 h at room temperature. The insoluble materials were removed by suction filtration, and the residue was rinsed twice with 20-mL portions of ether. The combined organic layers were concentrated in vacuo, and the trichloromethylcyclopentadiene was flash distilled under vacuum using a heat gun.

Triethylamine (2.73 g, 0.027 mol) was added to a cooled (ice bath) solution of the purified trichloride in 100 mL of ether. This mixture was stirred for 5 min at 0 °C, and the triethylamine hydrochloride which had formed was filtered off. The ether solution was washed three times with 30-mL portions of 10% hydrochloric acid, once with saturated sodium bicarbonate solution (30 mL), and once with water (30 mL). The organic extracts containing dichlorofulvene (**14**) were dried over Na_2SO_4 and concentrated to a volume of 40 mL in the presence of dimethyl azodicarboxylate (3.94 g, 0.027 mol). This mixture was stored at 4 °C until the Diels–Alder reaction was complete.

Any excess dimethyl azodicarboxylate could be removed by the following procedure. A solution of the crude adduct **15** in 200 mL of ether was placed in a 500-mL round-bottom flask equipped with a magnetic stirrer. Water (100 mL) was added, and the solution was cooled with stirring to 0 °C. Hydrazine hydrate (95%) was added slowly until all of the bubbling subsided. The resulting solution was washed several times with 75-mL portions of water and dried over Na_2SO_4. Concentration of the solvent afforded a yellow oil which was subjected to column chromatography on 50 g of Florisil. Elution with benzene provided pure dichlorofulvene dimer. By flushing the column with benzene/ethyl acetate (8:1), Diels–Alder adduct **15** which was pure by NMR spectroscopy could be obtained. Typical yields of **15** from nickelocene were 60–65%. Analytically pure adduct could be achieved by recrystallization from ether or ether/pentane.[35] NMR: δ 6.65 (t, 2 H, vinyl protons), 5.45 (bs, 2 H, bridgehead protons), 3.8 (s, 6 H, carbomethoxy protons).

Dimethyl 7-(Dichloromethylene)-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (16). The Diels–Alder adduct **15** (700 mg, 2.4 mmol) was dissolved in 50 mL of ethyl acetate and 40 mg of 10% palladium on charcoal was added. This solution was hydrogenated at atmospheric pressure until 1 equiv of hydrogen was taken up. The resulting mixture was filtered through Celite and the filtrate removed in vacuo to give the reduced product (700 mg, ~100%) as a dark red material. NMR: δ 4.95 (2 H, bs, bridgehead protons), 3.8 (6 H, s, carbomethoxy protons), 1.98 (4 H, bs, ethylene bridge protons).

7-Methylene-2,3-diazabicyclo[2.2.1]heptane (5). A solution of the hydrogenated adduct **16** (700 mg, 0.0024 mol) in 5 mL of ether was added to a degassed solution of potassium hydroxide (785 mg, 0.014 mol) in 20 mL of water under nitrogen. The resulting mixture was heated to 85–90 °C for at least 12 h. The solution was cooled, and 6 N hydrochloric acid was added to pH 1. Potassium carbonate was added to pH 9, and the solution was extracted with degassed chloroform. The combined organic layers were dried over $MgSO_4$ and concentrated to give the hydrazine (370 mg, 88%) as a solid brown material.

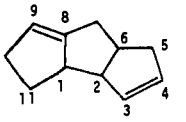


Table VIII

chemical shift, ppm	multiplicity	assignment
151.69	s	C-8
133.80	d	C-3 or C-4
129.80	d	C-3 or C-4
117.70	d	C-9
53.40	d	C-1 or C-2
53.20	d	C-1 or C-2
41.00	d	C-6
36.60	t	
32.78	t	
30.06	t	
25.89	t	C-11

This material (370 mg, 0.002 mol) was dissolved in ether (5 mL) and added to 30 mL of liquid ammonia at −30 °C (dry ice/2-propanol bath with a dry ice/acetone condenser). Sodium (195 mg, 0.009 mol) was added in small pieces until the blue color persisted, and then a drop or two of water was added to quench the excess sodium. The cold bath was removed and the ammonia allowed to slowly evaporate at room temperature. When almost all of the ammonia had evaporated, 5 mL of brine was added, and this solution was extracted with degassed chloroform. Utilizing the same work-up process as described in method A, one can obtain solutions of the desired azo compound **5** in 70–80% yield. Removal of the last traces of solvent by blowing nitrogen over the solution yielded **5** as a clear, colorless oil, which had the same NMR spectrum as that reported above.

Pyrolysis of 5 in Cyclopentadiene. A solution of diazene **5** (200 mg, 18.2 mmol) in 1.0 mL of freshly prepared cyclopentadiene was placed in a pyrolysis flask, degassed and sealed, and heated for 16 h at 60 °C. GC analysis of this solution on column D at 80 °C showed a multitude of peaks. Repeated preparative gas chromatography on column E at 100 °C gave the following clean adducts: peak 1 (retention time 55 min), cyclopentadiene dimer. Peak 2 (retention time 71 min): NMR δ 5.77 (m, 1 H, cyclopentene vinyl proton), 5.45 (m, 1 H, cyclopentene vinyl proton), 4.599 (s, 2 H, terminal methylene), 3.082 (m, 1 H, allylic methine proton), 2.20–2.60 (m, 5 H, allylic, bridgehead, and methine protons), 1.40 (m, 4 H, ethylene bridge protons); mass spectrum *m/e* 146 (parent), 131, 117, 91, 80 (base), 79, 77. Calcd for $C_{11}H_{14}$: 146.109 62. Found: 146.108 06.

The ^1H NMR spectrum of this material was identical with that of the authentically synthesized adduct **34** and thus the assignment given to this fraction is 10-methylene-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-ene.

Peak 3 (retention time 79 min): The ^1H NMR spectrum of a sample enriched with this material displayed a pair of one-proton multiplets at δ 6.01 and 5.96 and a broad one-proton singlet at δ 5.08. Based on this NMR data, we have tentatively assigned this peak as a F-1,2 product.

Peak 4 (retention time 95 min): The spectral data for this fraction were identical with those observed for authentically synthesized *syn*-B-1,4 adduct, 9-methylene-*exo*-tricyclo[4.2.1.$1^{2,5}$]dec-3-ene (**36**). NMR: δ 5.82 (s, 2 H, ring vinyl protons), 4.18 (s, 2 H, exo methylene protons), 2.45 (m, 2 H, allylic bridgehead protons on carbons 2 and 5), 2.22 (m, 2 H, allylic bridgehead protons on carbons 1 and 6), 1.75 (d, 1 H, J = 11 Hz, bridge proton on carbon 10), 1.49–1.69 (m, 4 H, ethylene bridge aliphatic protons), 1.20 (d of t, 1 H, bridge proton on carbon 10). Mass spectrum *m/e* 146 (parent), 131, 117, 105, 104, 91, 80, 79 (base), 77, 66. Calcd for $C_{11}H_{14}$: 146.109 62. Found: 146.107 85.

This material was dissolved in about 10–15 mL of methyl acetate, a spatula tip full of 10% palladium on charcoal was added, and the resulting mixture was hydrogenated overnight at atmospheric pressure. The reaction mixture was filtered through a Celite filled pipet,

Table IX. Product Distribution from the Thermolysis of **5** in Cyclopentadiene (CPD)

		products, %						
tube	[CPD],M	*endo*-B-1,2	*syn*-B-1,4	*anti*-B-1,4[a]	F-1,2a[b]	F-1,2b[b]	F-1,2d[c]	F-1,2c
1	12	7.1	14.4	1.8	27.2	14.4	3.9	31.0
2	6	8.3	9.4	1.3	39.2	14.8	4.2	21.6
3	4	9.4	5.9	0.7	43.0	18.6	5.5	15.4
4	1.2	10.9	2.7		52.1	17.9	4.8	11.0

[a] In most cases, the *anti*-B-1,4 peak was too small or broad to be accurately analyzed. [b] These peaks were not base line separated; therefore, the sum of the peaks is known more accurately than the percentage of each component. [c] This peak has been tentatively assigned as a F-1,2 adduct, although it was not isolated and no spectral data has been obtained for it.

Table X. Products of Photolysis of Diazene **5** in Neat Cyclopentadiene at 0 °C

retention time, min	%	assignment
27		cyclopentadiene dimer
29		cyclopentadiene dimer
37	0.5	F-1,2 adduct[a]
39	2.5	B-1,2 (exo) adduct **35**[a]
46	1.0	B-1,2 (endo) adduct **34**[b]
48	34.0	B-1,4 (syn) adduct **36**[b]
59	2.0	B-1,4 (anti) adduct **37**
62		F-1,2 adduct[c]
64	17.0	F-1,2 adduct[c]
73	42.0	F-1,2 adduct

[a-] These peaks were not base line separated; the sum of the peaks is known more accurately than the percentage of each component.

and the solvent removed by distillation through a 6-in. Vigreux column until ~1 mL remained. VPC analysis of this solution on column D at 90 °C showed the presence of two nonsolvent peaks. Preparative gas chromatography on column E at 100 °C cleanly separated the two components. The second fraction corresponded to unreacted starting material. However, the first fraction (retention time 50 min, column D, 90 °C) had spectral data which were identical with those obtained for authentically synthesized *exo*-9-methylenetricyclo[4.2.1.$1^{2,5}$]-decane (**55**) (Scheme IX). NMR: δ 4.56 (s, 2 H, methylene vinyl protons), 2.23 (bs, 2 H, allylic bridgehead protons), 2.06 (bs, 2 H, bridgehead protons), 1.3-1.73 (m, 9 H, aliphatic protons), 1.03 (d of t, 1 H, J = 11 Hz, bridge proton). Mass spectrum: *m/e* 148 (parent), 133, 119, 91, 81, 80 (base), 66, 44. Calcd for $C_{11}H_{16}$: 148.125 28. Found: 148.124 46. Therefore fraction 1 is the monohydrogenated product.

Peak 5 (retention time 102 min): This fraction was not completely purified by preparative GC analysis, but the ^{1}H NMR spectrum of a sample enriched with this component indicated singlets at δ 6.28 and 4.48. These resonances are consistent with the structure of the *anti*-B-1,4 adduct **37.**

Peak 6 (retention time 106 min): NMR δ 5.72 (m, 1 H, cyclopentene vinylic proton), 5.60 (m, 1 H, cyclopentene vinylic proton), 5.25 (bs, 1 H, fused ring vinyl proton), 2.90 (m, 1 H, allylic methine proton), 2.61 (m, 2 H, allylic protons), 2.50 (m, 4 H, allylic protons), 2.23 (d of t, 2 H, J = 13 Hz, methine proton), 1.79 (m, 1 H, aliphatic ring proton), 1.47 (m, 1 H, alipahatic ring proton); mass spectrum *m/e* 146 (parent), 131, 117, 91, 81, 80, 79, 66. Calcd for $C_{11}H_{14}$: 146.109 62. Found: 146.108 77. This spectral data is indicative of a tricyclo[6.3.$0^{1,8}$.$0^{2,6}$]undecadiene system which is representative of fused 1,2 (F-1,2) cycloadduct formation.

Peak 7 (retention time 112 min): NMR δ 5.65 (m, 1 H, cyclopentene vinyl proton), 5.60 (m, 1 H, cyclopentene vinyl proton), 5.21 (bs, 1 H, fused ring vinyl proton), 3.48 (m, 1 H, allylic methine proton), 1.25-2.52 (m, 10 H, allylic and aliphatic protons); mass spectrum *m/e* 146 (parent), 131, 117, 90, 81, 80, 79, 66. Calcd for $C_{11}H_{14}$: 146.109 62. Found: 146.108 87. This spectral data is also indicative of a fused 1,2 (F-1,2) type cycloadduct of the tricyclo[6.3.$0^{1,8}$.$0^{2,6}$]-undecadiene series.

Peak 8 (retention time 155 min): NMR δ 5.65 (m, 1 H, cyclopentene vinyl proton), 5.57 (m, 1 H, cyclopentene vinyl proton), 5.25 and 5.24 (s, 1 H, fused ring vinyl proton), 3.44 (m, 1 H, allylic methine proton), 3.16 (m, 1 H, allylic methine proton), 2.7 (m, 1 H, allylic proton), 2.51 (m, 2 H, allylic protons), 2.20 (m, 3 H, allylic protons), 2.0 (m, 2 H, methine plus ring protons), 1.55 (m, 1 H, ring proton). Mass spectrum: *m/e* 146 (parent), 121, 91, 90, 80, 79, 66, 55, 53. Calcd for $C_{11}H_{14}$: 146.109 62. Found: 146.110 54. This also appears to be a fused 1,2 (F-1,2) product. The ^{13}C NMR spectrum in 0.05 M $Cr(AcAc)_3$ with 5-s pulse delay is given in Table VIII.

Dilution Study. Pyrolysis of Diazene 5 with Cyclopentadiene. Azo compound **5** (200 mg, 1.85 mmol) was added to a 1-mL volumetric flask and diluted to the mark with freshly distilled cyclopentadiene. Four pyrolysis tubes were made up by diluting with the appropriate amount of acetonitrile. The tubes were degassed and sealed as described previously.

The tubes were heated overnight at 60-65 °C. They were then opened and the mixture was analyzed on column D at 80 °C with a flow of 2.5. The results are summarized in Table IX.

Photolysis of Azo Compound 5 in Cyclopentadiene. A solution of 20 mg (0.18 mmol) of diazene **5** in 150 μL of neat cyclopentadiene was placed in a Pyrex tube, degassed and sealed, and photolyzed at 0 °C for 4 h in the Rayonet with 16 lamps (350 nm). The reaction tube was opened, the excess cyclopentadiene was removed by blowing a stream of nitrogen over the solution, and the residue was analyzed by GC on column O at 80 °C. The results are given in Table X.

The assignment of these peaks was made by comparison to their relative retention times on column D (80 °C), and also by coinjection studies with authetically synthesized adducts, along with ^{1}H NMR spectra of isolated fractions.

GC-mass spectral analysis of the first two emergent peaks (retention times 37 and 39 min) has shown that these are TMM-derived cycloadducts (parent *m/e* 146). The first emerging component was assigned as a F-1,2 isomer, since these were the only types of cycloadducts unaccounted for. This material could be the same F-1,2 isomer as the second emerging material which was isolated in the pyrolysis runs, or it could be different F-1,2 diene.

The second emerging component (retention time 39 min) was found

Table XI. Product Distribution from the Photolysis of **5** in the Presence of Cyclopentadiene

		products, %						
tube	[CPD], M	F-1,2d[a]	*exo*-B-1,2[a]	*endo*-B-1,2[b]	*syn*-B-1,4[b]	*anti*-B-1,4	F-1,2 $\beta + \gamma$[c]	F-1,2δ
5	2.2	0.9	4.3	1.6	36.4	2.1	18.0	36.6
6	1.1	1.2	7.9	2.4	33.4	2.1	18.9	33.1
7	0.22	5.5	9.1	2.7	26.3	2.7	21.3	32.4
8	0.11	14.4	8.6	3.2	18.1	5.1	23.6	27.0
9	0.055	21.0	10.7	2.4	9.8	5.5	27.5	23.1

[a,b] These peaks were not base line separated; the total sum of the peaks is known more accurately than the relative percentage of each component. [c] This percentage is the sum of two peaks which were not base line separated.

to have the same retention time (by coinjection) as the authentically synthesized *exo*-B-1,2 diene **35**. While the ^{1}H NMR spectrum of a sample enriched with this component showed the presence of signals attributable to **35**, these were very weak relative to cyclopentadiene dimer resonances. Thus, this component contains some B-1,2 exo diene **35** along with other as yet unidentified material.

The material which emerges at a retention time of 59 min was assigned as the *anti*-B-1,4 diene **37**. Coinjection of authentically synthesized F-1,4 dienes, **38** and **39**, with the crude reaction mixture demonstrated that these isomers have the same relative retention time (59 min) as the aforementioned *anti*-B-1,4 isomer. However, ^{1}H NMR analysis of a sample enriched in this component showed only those resonances attributable to the *anti*-B-1,4 diene **37**. No signals corresponding to either of the F-1,4 dienes, **38**, and **39**, were observed.

Dilution Study. Photolysis of Diazene 5 with Cyclopentadiene. A solution of 30 mg (0.23 mmol) of **5** in 200 μL (2.2 mmol) of cyclopentadiene was diluted to the mark with acetonitrile in a 1-mL volumetric flask. Five tubes were made up using the appropriate amount of stock solution and acetonitrile. The tubes were degassed and sealed as described previously and photolyzed at 0 °C for 8 h in the Rayonet with 16 lamps (350 nm). They were then opened and analyzed on column O at 80 °C. The results are given in Table XI.

Photolysis of Azo Compound 5 in Cyclopentadiene-d_6. A solution of ~20 mg (0.18 mmol) of diazene **5** in 500 μL of perdeuteriocyclopentadiene[38] was carefully sealed in a degassed NMR tube and photolyzed at 0 °C using 16 350-nm lamps.

The ^{1}H NMR spectrum (Bruker, 270 MHz) of the starting solution clearly showed the signals for both the exocyclic methylene protons and the bridgehead hydrogens of **5**. After 1 h of irradiation, the ^{1}H NMR spectrum (probe at 0 °C) of the solution indicated that ~50% (relative to vinyl region of protiocyclopentadiene present in d_6 material) of the azo compound had already decomposed. After 2.5 h of irradiation, the decomposition of the diazene was essentially complete, since no signals attributable to the starting azo compound **5** could be detected in the ^{1}H NMR spectrum.

Therefore, under the typical reaction conditions and amounts of diazene **5** used in our photolysis experiments, it is safe to assume that 8 h of irradiation is more than sufficient to effect complete deazetation of the azo compound.

Material Balance of Cycloadducts in the Photolysis of Diazene 5 in Cyclopentadiene. A mixture of ~20 mg of azo compound **5**, 20.7 mg (0.12 mmol) of dodecane, and 1 mL of cyclopentadiene was placed in a specially stopcocked Pyrex tube, degassed and sealed, and photolyzed for 8 h at 0 °C with 16 350-nm lamps. The reaction tube was then cooled to 77 K, and the quantity of N_2 liberated during the reaction was measured on a Toepler pump until a constant reading was observed. In this way an accurate yield of the amount of starting azo compound could be determined. In this case, 8.0 mg (0.074 mmol) of diazene **5** was present in the reaction mixture.

GC analysis of this mixture on column D at 90 °C provided clean separation of the cycloadducts and dodecane, and no dimer formation (<2%) was observed. The yield of cycloadducts was determined by the following equations:

$$\text{mol}_{\text{exptl}}\ \text{adduct} = (\text{area adduct}/\text{area dodecane}) \times \text{detector response} \times \text{wt dodecane}$$

$$\text{mol}_{\text{calcd}}\ \text{adduct} = \text{mol wt adduct} \times \text{mol of } \mathbf{5}$$

$$\text{yield} = \text{mol}_{\text{exptl}}/\text{mol}_{\text{calcd}} = 97.2\%$$

Control Reaction to Check for F-1,4 Adducts in the Dilute Pyrolysis of Azo Compound 5 in Cyclopentadiene. Because no products corresponding to the authentically synthesized fused 1,4 (F-1,4) adducts **38** and **39** were observed in the pyrolysis of photolysis reactions of diazene **5** in neat cyclopentadiene, an attempt was made to detect these products by running a very dilute pyrolysis reaction. A stock solution (200 μL) that was ~1 M azo compound **5** in cyclopentadiene was diluted with 100 mL of acetonitrile and pyrolyzed under nitrogen for 16 h. The triplet-product enriched reaction mixture was analyzed on column D at 90 °C, and a mixture of peaks with retention times encompassing those of the F-1,4 adducts **38** and **39** was isolated by preparative GC on column E at 100 °C. NMR analysis of this mixture indicated the presence of the already characterized fused 1,2 (F-1,2) cycloadducts and the (F + B) dimer. No resonances corresponding to the F-1,4 adducts **38** and **39** were observed.

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Supplementary Material Available: Experimental procedures for the synthesis and characterization of the substances shown in Schemes I-III, V, VII-IX, and XI (27 pages). Ordering information is given on any current masthead page.

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