Influence of the Geminal Biscyclopropyl Group in the Reactions of Trimethylenemethane: Reversible Intersystem Crossing

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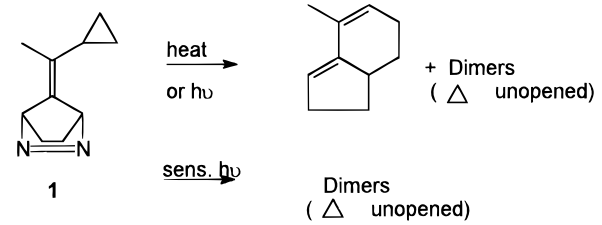
The azo compound precursor to Berson's trimethylenemethane (TMM) biradical system, 2-methylene-1,3-cyclopentanediyl, was substituted with two cyclopropyl groups on the exomethylene. Generation of the TMM species by pyrolysis, direct photolysis, and benzophenone-sensitized photolysis resulted in formation of both cyclopropane ring-opened monomer and cyclopropane ring-unopened dimers whose ratio depended directly on temperature and extent of dilution. The ground state appears to be triplet on the basis of ESR spectrometry. The results contrast with previous work (Waldemar Adam) showing that monocyclopropyl substitution on Berson's TMM species gives both ring-opened monomer and ring-unopened dimers upon pyrolysis and gives mostly ring-unopened dimer upon direct photolysis at 0−20 °C in what appear to be concentration-independent reactions. The observations with the biscyclopropyl-substituted species are consistent with steric effects retarding dimerization of the triplet allowing reversible intersystem crossing back to singlet and perhaps with reduction in the singlet−triplet gap as well.

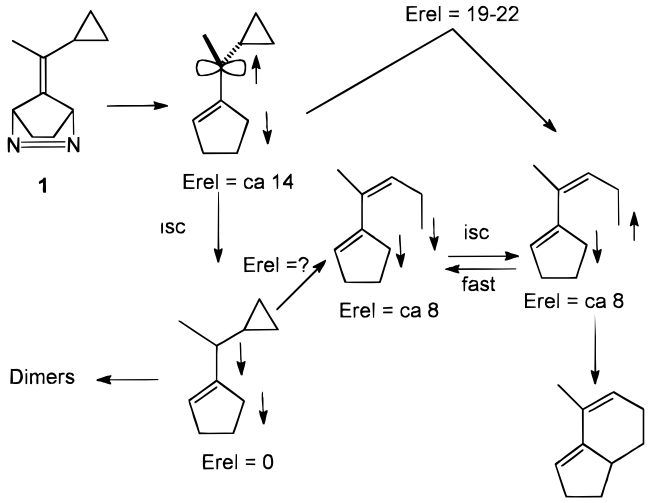
The determination of electron multiplicity in cross-conjugated organic biradical systems is an important pursuit and is one which is made more difficult if the species cannot be generated under matrix isolation conditions and studied by electron spin or optical spectroscopy. The tetramethyl-*m*-xylylene generated by isobutylidene addition to dimethylfulvene[1] is one such case. Our recent work[2] has shown that addition of dioxygen suppresses formation of the dimeric product while not inhibiting generation and reaction of isobutylidene. Unfortunately, both singlet and triplet biradicals are known to react with oxygen so a distinction cannot be made between spin states on the basis of reactivity with oxygen except by comparison with some other reaction that clearly indicates the presence of at least two intermediates.

Waldemar Adam recently introduced the criterion of ring opening of cyclopropyl-substituted cross-conjugated biradicals as evidence for involvement of singlet states.[3] Thus, thermal and direct photolysis of a cyclopropyl derivative of Berson's azo compound precursor[4] to TMM, **1**, gives monomeric product resulting from cyclopropylcarbinyl radical rearrangement and closure along with cyclopropane ring-unopened dimers—all as a function of temperature—but triplet sensitized photolysis gives almost exclusively dimeric products with no cyclopropane ring opening (Scheme 1).

Scheme 1



Scheme 2



It was recognized (a) that the ring-opened singlet biradical would be roughly 6 kcal/mol more stable than the most stable singlet TMM species which has an orthogonal π system, (b) that the ring-opened triplet biradical would have nearly the same energy as the singlet since the radical sites are not coupled directly, and (c) that the planar triplet TMM has been calculated to be 14 kcal/mol more stable than the perpendicular singlet.[3] It was then suggested that the activation energy for cyclopropylcarbinyl radical ring opening (ca. 5−8 kcal/mol, see below) must be added to the difference in energy between the triplet TMM and the ring-opened triplet so that the overall preference for ring opening from singlet was greater than that from triplet TMM (Scheme 2). It should be noted here that the relative activation energies for ring opening in the two states may not be as relevant as the rate of ring opening vs intersystem crossing in the

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(1) Gajewski, J. J.; Chang, M. J.; Stang, P. J.: Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 2096.

(2) Gajewski, J. J.; Paul, G. C.; Chang, M. J.; Gortva, A. M. *J. Am. Chem. Soc.* **1994**, *116*, 5150.

(3) Adam, W.; Finzel, R. *J. Am. Chem. Soc.* **1992**, *114*, 4563.

(4) (a) Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. *J. Am. Chem. Soc.* **1971**, *93*, 1544. (b) Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 276. See also: Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, **1982**; pp 151−194. (c) Berson, J. A. In *The Chemistry of Quinonoid Couponds*, Vol. II; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd: New York, 1988; pp 481−485. (d) Rule, M.; Mondo, J. A.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2209. (e) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2217. (f) Closs, G. L. *J. Am. Chem. Soc.* **1971**, *93*, 1546.

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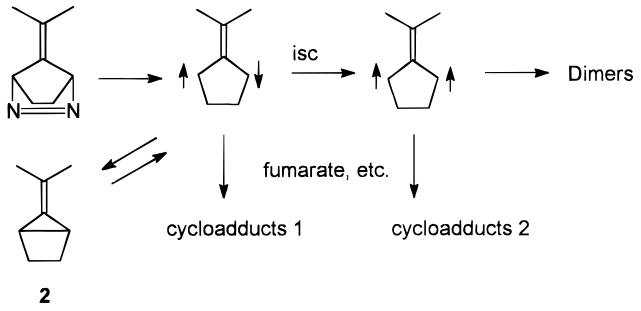
Scheme 3



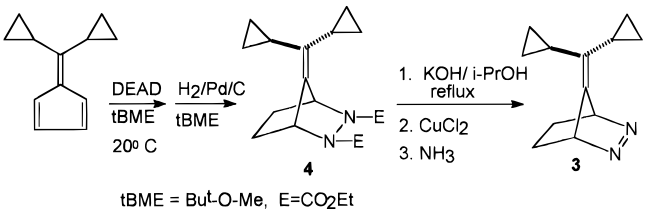
singlet state and the relative rate of ring opening vs dimerization in the triplet state; thus the relative rates of ring-opening in either state may be irrelevant.

There can be little doubt that both singlet and triplet trimethylenemethane biradicals are involved in the deazetization of **1**, and in the corresponding geminallyl-substituted dimethyl case Berson observed differential trapping of at least two different intermediates by fumarate as a function of concentration.[4b] And one of these cannot be the ring-closed hydrocarbon, 5-isopropylidenebicyclo[2.1.0]pentane, **2**, since the trapping reaction of this species does not occur directly but via an intermediate which is most likely one of the TMM biradical species.[4e] Further, the ring-closed hydrocarbon gives dimers at −55 °C (the same dimers as found in the deazetizations) via a first-order reaction which has a preexponential term consistent with reversible ring opening and rate-determining intersystem crossing.[4d] Finally the formation of dimers is accompanied by CIDNP signals which almost certainly require a triplet precursor.[4f] The reaction pathways of Scheme 3 involving an irreversible cascade of a singlet to a triplet TMM species are consistent with the observations and kinetic data.

It should be noted, however, that at higher temperatures closure of the singlet biradical to the ring-closed hydrocarbon is fast compared with intersystem crossing but at low temperatures ring closure is slow compared with intersystem crossing. This occurs because the intersystem crossing rate is relatively temperature independent, but ring closure apparently has a finite activation energy barrier. Finally, it must be recognized that the intersystem crossing described in Scheme 3 must be irreversible or effectively so. If this were not the case then the ratio of product derived from singlet TMM (cycloadducts 1 from Scheme 3 or ring-opened monomer of Scheme 2) and product derived from triplet TMM (dimers or cycloadducts 2 from Scheme 3) would necessarily change with initial concentration. In trimethylenemethane chemistry, reversible intersystem crossing has not be observed, although it was suggested by Dowd[5] with the parent case where the major product from low-temperature photolysis of 4-methylenepyrazoline is methylenecyclopropane under conditions where the sample gives a triplet ESR spectrum. His suggestion therefore is that the triplet must undergo intersystem crossing back to singlet before closing, provided, of course, that the ESR-active species is actually responsible for monomeric methylenecyclopropane product. With such considerations in mind, an effort was made to examine the response of a TMM biradical system to more sterically demanding substitution like that derived from **3**.

(5) Dowd, P.; Chow, M. *J. Am. Chem. Soc.* **1977**, *99*, 6438. It is of some concern here that both the activation parameters for the loss of ESR signal intensity are low, suggesting that intersystem crossing occurs, but the activation energy is much too low relative to that expected on the basis of high level calculations (14 kcal/mol: see ref 7). It may be that the loss of ESR intensity does not give the major product which itself can result from closure of the initially formed singlet trimethylenemethane species.

Scheme 4



Results

Synthesis of Diazene 3. Diazene **3** was synthesized by standard procedures[3] following Scheme 4. Diethyl azodicarboxylate (DEAD) adds in a Diels−Alder fashion to the fulvene to give the adduct(s). Reduction of the endocyclic double bond by catalytic hydrogenation resulted in the formation of the biscarbamate. Hydrolysis with KOH in refluxing *i*-PrOH and oxidation with $CuCl_2$/NH_3 afforded diazene **3**. Compound **3** is labile and slowly decomposes at room temperature.

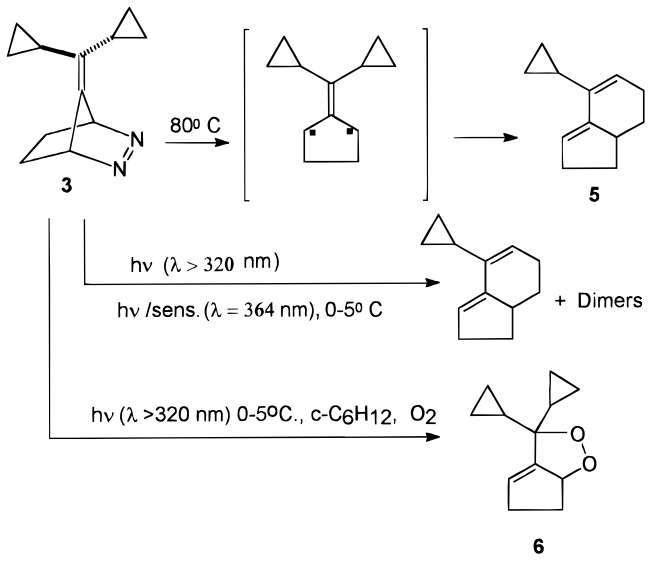
Thermolysis and Photolysis of 3. Thermolysis of diazene **3** in benzene solvent in a vacuum degassed sealed tube (boiling water bath) resulted in the formation of only monomeric rearranged hydrocarbon 2-cyclopropylbicyclo-[4.3.0]nona-1(9), 2-diene, **5** (Table 1 and Scheme 5). No dimers or any other products were formed in detectable amounts. Furthermore, an NMR sample left in chloroform-*d* at room temperature gave only ring-opened monomer. Photolysis of **3** in a benzene solution at 0−5 °C, however, gives both monomeric product **5** and $C_{24}H_{32}$ dimers in roughly a 1:1 ratio. Direct photolysis starting with a sample twice as dilute in benzene gives relatively more ring-opened monomer (ratio monomer to dimer = 2.85:1). No attempt was made to determine the ratio as a function of percent reaction since it is clear that this should vary over the course of the reaction whereas the total product provides an integration of this ratio. Triplet-sensitized photolysis (benzophenone irradiation from an argon ion laser at $\lambda = 364$ nm to avoid direct irradiation of **3**) generates dimers and ring-opened monomer. NMR spectrometry also revealed that the dimers possessed intact cyclopropane rings since the vinyl proton to secondary cyclopropane ring proton ratio is roughly 15, which is characteristic of a mixed bridged-fused dimer or a 1:1 mixture of fused and bridged dimer or an indeterminant mixture of both possibilities by analogy to previous work.[4a] Further, direct photolysis at −78 °C in $CFCl_3$ gives only ring-unopened dimers. Finally direct photolysis of the diazene in cyclohexane which was saturated with oxygen gas gave no hydrocarbon product; however, the residue of the reaction was chromatographed to give a material whose NMR spectrum is consistent with 4,4-di(cyclopropyl-2,3-dioxabicyclo-[3.3.0]oct-5-ene, **6**. An unidentifiable material with a higher R_f is also present in smaller amounts, but it could not be isolated. However, its proton resonances in the reaction mixture occur at δ 2.6, 2.55, 1.1, 0.6, and 0.3. Thus, it is not a ring-opened monomeric peroxide like that observed as a minor product by Adam in the thermolysis of his methylcyclopropyl azo compound in the presence of oxygen. Table 1 lists the results of experi-

Table 1. Product Distribution from Berson's Azo Compound TMM Precursor with Methylcyclopropyl and Biscyclopropyl Substitution

	methylcyclopropylTMM[d]		biscyclopropyl TMM[e]		
conditions	fraction monomer[a]	fraction dimer[b]	fraction monomer[a]	fraction dimer[b]	unrearr. peroxide
80−100 °C	0.59	0.41	1.0.	0.0	
hν, 0 °C	0.09	0.86	0.5	0.5	
2× dilution			0.74	0.26	
hν, 20 °C, O_2	0.15	0.0			0.85
hν, 0 °C, O_2			0.0	0.0	major prod.
hν, 0 °C, Ph_2CO	0.02	0.98	ca. 0.55	ca. 0.45	
hν, −78 °C	0.02 + housane[c]	0.85	0.0	1.0	

[a] Cyclopropane ring-opened monomer. [b] Intact cyclopropane rings in dimers. [c] The housane goes exclusively to dimers upon warming. [d] From Adam's compound, ref 3. [e] Compound **3** this work.

Scheme 5



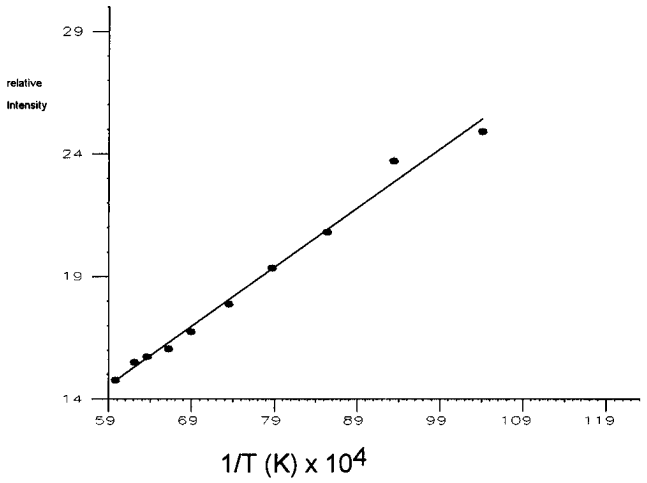


Figure 1. Curie plot from the ESR spectrum of the photolysis of **3** in a propylene glycol matrix.

ments reported here that can be compared to those reported by Adam on the monocyclopropyl azo compound.[6]

ESR Studies of the Biscyclopropyl TMM Species Derived from 3. Concern about the multiplicity of the ground state of the biscyclopropyl TMM species being generated prompted examination of the ESR spectrum of the photolysate of **3** at low temperatures in viscous matrices. At 77 K in methyltetrahydrofuran, an ESR spectrum was obtained that was characteristic of a randomly oriented, rotationally frozen triplet species looking identical to that first observed by Berson with the dimethyl derivative.[4a] For the triplet derived from **3**, $|D|/hc$ equals 0.0232 cm^{-1} and $|E|/hc$ equals 0.00234 cm^{-1}. In addition, a half-field absorption was also observed. At higher temperatures in both methyl-THF and in 1- and 2-propanol mixtures, the triplet spectrum collapsed to a more narrow line with hyperfine splitting at the position expected for a doublet, and this spectrum disappeared upon warming above 128 K. In a propylene glycol matrix, the triplet spectrum did not collapse until higher temperatures. The ESR intensity increased at lower temperatures, and indeed, a linear Curie plot was obtained from 167 to 96 K (see Figure 1). This behavior is characteristic of a ground state triplet or of a singlet−triplet equilibrium where it can be calculated that the singlet is no lower than ca. 0.3 kcal/mol below the triplet.[4c] Upon warming to room temperature, only ring-unopened dimers were found by NMR spectrometry.

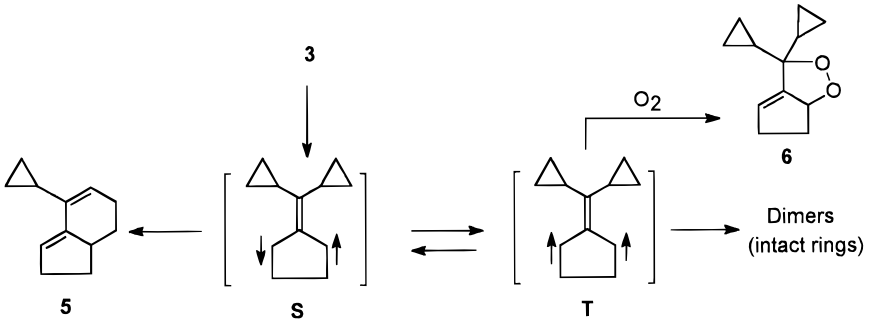
Discussion

The results shown in Table 1 clearly indicate a concentration dependence in the product distribution when reactions are conducted at the same temperature using the same energy source. However, comparison of the relative amounts of ring-opened product and dimer under one set of reaction conditions with another is difficult. The dimerization rate of the biradicals depends on the concentration of the biradicals, and this changes not only with temperature and the energy source but necessarily during the course of the reaction. So photolysis at 0 °C can generate a higher concentration of biradicals than pyrolysis at 80 °C from precursor **3** at any given time during a reaction. Nonetheless, the results described in Table 1 make it clear that 6,6-dicyclopropyl substitution on the TMM species has a profound effect on the energy surface of the TMM system since the product distribution (cyclopropane rearranged

(6) Attempts were made to trap the TMM species from **3** with dimethyl fumarate under the photolysis conditions (see ref 4b), but there was rapid conversion of fumarate to maleate in photolyses conducted in acetonitrile solvent even upon irradiation through Pyrex in a reaction reminiscent of that reported by Albone (Albone, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 4663). In contrast, pyrolysis of **3** in the presence of dimethyl fumarate (two experiments with a ca. 20-fold difference in concentration) gave both ring-opened monomer and at least two fumarate adducts (HRMS for $C_{18}H_{24}O_4$: calcd 304.1674; found 304.1675). From the NMR in the vinyl proton region, there appear to be two fused adducts in a 1:1 ratio with the ratio of monomer to adducts being approximately 11-fold higher in the more dilute case. However, the GC reveals the presence of two peaks with the appropriate masses for adducts in a 1:1.75 ratio consistent with the presence of a bridged adduct coeluting with one of the fused adducts. Despite the incomplete characterization of these adducts, it is important to note that their relative proportions did not change with concentration of starting material and fumarate, unlike that reported in ref 4b.

(7) Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 967. Davidson, E. R., private communication.

Scheme 6



Scheme 7

monomer to dimers) varies with the initial concentration of azo compound precursor.

A number of hypotheses can be entertained to account for the difference resulting from biscyclopropyl substitution: (A) steric retardation of the dimerization which would either allow reversible intersystem crossing to form singlet which ring opens (variation A1, Scheme 6) or allow ring opening out of triplet (variation A2, Scheme 7)[8] or (B) reduction in the size of the singlet−triplet gap by destabilizing the planar triplet[9] which would permit reversible intersystem crossing relative to dimerization, thus forming a singlet which undergoes ring opening.

It might also be argued that biscyclopropylcarbinyl radicals might undergo increased rates of ring-opening relative to monocyclopropylcarbinyl radicals, and this would rationalize the increased amount of ring-opened monomeric product with **3** relative to the methylcyclopropyl case studied by Adam;[3] however, the concentration dependence could not be rationalized by this. Further, studies by Beckwith reveal little difference in the rate of ring opening of cyclopropylcarbinyl radical in the mono- or dicyclopropyl-substituted parent systems.[10,11]

Other mechanistic alternatives include formation of the ring-closed biscyclopropyl-substituted 5-isopropylidenebicyclo[2.1.0]pentane which for no obvious reason undergoes both unimolecular cyclopropane ring-opening and rearrangement and bimolecular dimerization in contrast to the systems studied by Berson and by Adam. It is also possible that the one-bond-broken diazene biradical might be involved, and it could undergo the cyclopropylcarbinyl radical cleavage before loss of nitrogen and give rearranged monomer after nitrogen loss. It might also be responsible for formation of a triplet TMM species and at the same time react with the TMM triplet to give dimer precursors. However, this behavior must have resulted from the bis-geminal cyclopropyl substitution again in contrast to the Berson and Adam systems for reasons that are not obvious. Finally, it is possible that the Adam supposition of a higher activation energy for ring opening of the triplet TMM species than for the singlet TMM species is not correct and that ring opening of triplet TMM with an activation energy of roughly 7 kcal/mol cannot compete with dimerization except in the case of substitution with larger groups. This is formally equivalent to Scheme 7 with the substitution of rapid interconversion of singlet and triplet ring-opened biradicals for rapid intersystem crossing in the TMM biradicals.

If the last possibility were correct, then none of the results reported here bear on the question of intersystem crossing in the TMM biradical; they merely refer to the perturbation introduced by the bis-geminal cyclopropyl substitution. That this possibility is not viable can be deduced from consideration of the *trans* isomer of the ring-opened biradical. Given Adam's scheme (Scheme 2) the ring opening of the singlet TMM species can occur to give both a *cis* and a *trans* allylcarbinyl radical, but it is only the *cis* one which can ring-close to the monomeric product. Therefore the *trans* one must return to its singlet TMM precursor (E_{act} = 11−14 kcal/mol, see Scheme 2) to be recycled back to the *cis* allylcarbinyl ring-opened biradical. However, intersystem crossing of the *trans* ring-opened singlet to triplet should be fast, and it can close to the triplet TMM species. Since high-temperature reactions result in mostly or exclusively ring-opened monomer in the mono- and bis cyclopropyl cases, respectively, with little or no dimer being formed, the transition state energy for closure of the *trans* triplet biradical (to give triplet TMM and ultimately dimer) must be higher in energy than the transition state for ring-opening of the singlet TMM species to the *cis* allylcarbinyl species (Scheme 8). This not only places the transition state for the ring-opening of the triplet TMM above the transition state for ring-opening of the singlet but also higher than that for intersystem crossing at lower temperatures.[12] It is therefore true that the only possible scheme consistent with all the facts at lower temperatures is that described in Scheme 6 which involves reversible intersystem crossing. Apparently, it is the reduction in the rate of dimerization of the bis-geminal cyclopropyl substituted species which allows this.

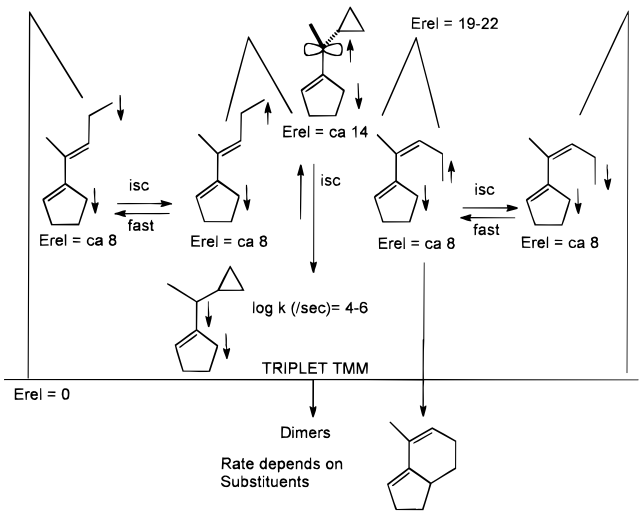
(8) A variation on this hypothesis is reaction exclusively out of the singlet state. This would appear to require either that the singlet be much more stable than the triplet or that all reactions are faster with the singlet than the triplet. The ESR argues against a singlet ground state of substantially greater stability than the triplet, and diradical trapping by oxygen and by dimerization appear to be diffusion-controlled processes with triplet biradicals but not with singlet biradicals or biradicaloids (Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Scaiano, J. C.; Berinstain, A. B.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1993**, *115*, 8073) so that exclusive singlet reactivity is hard to justify.

(9) Salinaro, R. F.; Berson, J. A. *Tetrahedron Lett.* **1982**, 1447, 1451.

(10) Beckwith, A. L. J.; Bowry, V. W. J. Am. Chem. Soc. **1994**, *116*, 2710. Ring opening of the biscyclopropylcarbinyl radical has log k (s^{-1}) = 13.9−8600/RT ln 10, and ring opening of methylcyclopropylcarbinyl radical has log k (s^{-1}) = 13.1−7700/RT ln 10. At 0 °C both radicals open with the same rate. Over the temperature range studied here, the largest rate difference is a factor of 2. See also: Lemieux, R. P.; Beak, P. *J. Org. Chem.* **1990**, *55*, 5454, where a dicyclopropylcarbinyl radical ring opens a factor of 4 slower than a monocyclopropyl radical where both are spiro to a 3-indanyl radical.

(11) It should be noted that Adam suggests that ring-opening must have an activation energy of only 5 kcal/mol to make it competitive with intersystem crossing in the methylcyclopropyl-substituted case.

Scheme 8



Just why the triplet energy surface is as described above is not clear, nor is it obvious that the dimerization would be so dramatically inhibited by the presence of a second cyclopropyl group unless there are specific geometric requirements for the reactions on the triplet surface.

Lastly, there should be some concern about possible steric effects on the singlet−triplet gap in the bis cyclopropyl-substituted TMM species derived from **3**. Modified INDO calculations by Lahti have revealed a 2−3 kcal/mol contraction in the gap presumably due to steric destabilization of the planar triplet.[13] This, however, does not dramatically alter any of the considerations above.

Conclusion

An important observation is the fact that bis-geminal cyclopropyl substitution on the trimethylenemethane biradical reduces the extent of dimerization and increases the extent of cyclopropane ring-cleavage relative to monocyclopropyl substitution. The observations are best rationalized by steric retardation of dimerization by triplet and perhaps reduction in the singlet−triplet gap. The retardation of dimerization of moderately stable triplet states then allows reversion to the singlet TMM which undergoes ring opening.

Experimental Section

Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Varian VXR-400 MHz instrument. All chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and were taken in chloroform-d solution. High-resolution mass spectra (HRMS) were recorded on a KRATOS MS-80/RFAQ spectrometer.

6,6-Dicyclopropylfulvene. 6,6-Dicyclopropylfulvene was synthesized from sodium metal (1.8 g, 0.08 mol), absolute ethanol (40 mL), dicyclopropyl ketone (0.08 mol), and freshly distilled cyclopentadiene (6.7 mL) according to literature procedures.[14] After stirring at room temperature (overnight), the mixture was treated with 110 mL of water. The organic layer was separated, and the aqueous layer was extracted (CH_2Cl_2, 50 mL × 3). The combined organic layer was washed with water until washings were neutral and dried over anhydrous sodium sulfate. The methylene chloride was removed under aspirator vacuum. Fractional distillation at ∼15−8 Torr gave a yellow orange fraction (3.8 g, bp 100−120 °C) having 90% of the desired fulvene contaminated with starting ketone (∼8.5%). A pure sample of the dicyclopropylfulvene was obtained upon silica gel flash chromatography (5% ether in pentane). ^{1}H NMR: δ 6.69 (m, 2 H), 6.46 (m, 2 H), 1.83 (m, 2 H), 1.05−0.84 (m, 8 H).

2,3-Dicarbethoxy-7-(2,2-dicyclopropylmethylidene)-2,3-diazabicyclo[2.2.1]heptane (4). Following the general procedures for the synthesis of cyclopropyl methyl-substituted diazene by Adam and Finzel,[3] **4** was synthesized from dicyclopropylfulvene (0.57 g, 3.61 mmol), diethyl azodicarboxylate (0.636 g, 3.65 mmol), and *tert*-butyl methyl ether (10 mL) at 20 °C followed by reduction of the endocyclic double bond by catalytic hydrogenation over palladium−carbon (5%, 40 mg). Chromatography (70% EtOAc, 30% pentane) over silica gel gave a viscous liquid (∼1.0 g) as a moderately pure sample. ^{1}H NMR: δ 5.05 (bd, 2 H), 4.20 (bs, 4 H), 1.9 (bs, 2 H), 1.26 (m, 10 H), 0.70−0.40 (m, 8 H). MS: 334 (M^+, 100), 261 (22), 234 (33), 189 (25), 159 (70), 117 (46), 91(28). HRMS for $C_{18}H_{26}N_2O_4$: calcd 334.1892, found 334.1902.

7-(2,2-Dicyclopropylmethylidene)-2,3-diazabicyclo[2.2.1]-hept-2-ene (3). Compound **4** (∼1.0 g) was hydrolyzed with KOH (1.55 g) in 2-propanol (16 mL) followed by oxidation via a copper complex as is described for monocyclopropyl-substituted diazene[3] to give the desired diazene **3**. This was purified by flash chromatography (ether/pentane, 1:1) over silica gel. ^{1}H NMR: δ 5.58 (t, J = 1.6 Hz, 2 H, bridgehead H), 1.63 (m, 2 H, Hexo), 1.20 (tt, J = 8.4 and 5.6 Hz, 2 H, cyclopropyl H), 1.08 (m, simulated J = 10, 5.2 and 3.8 Hz, 2 H, Hendo), 0.62 (m, 4 H), 0.49 (m, 4 H). ^{13}C NMR: 128.37, 73.96, 21.23, 12.62, 4.81, 4.79. UV (PhH) λ_{max} 340 nm (log ϵ = 2.13); $\epsilon \cong 4$ at 360−365 nm. CIHRMS for $C_{12}H_{16}N_2$: calcd for $M^+ + 1$ 189.1391, found 189.1396.

Thermolysis of Diazene 3. A small amount of diazene (8−10 mg) taken in a glass tube containing benzene (1.5 mL) was degassed (freeze−pump−thaw cycle (3 times)) and sealed under vacuum. After the sample was heated in a boiling water bath for 20 min, the contents of the tube were analyzed by GC and GC−MS, showing basically one compound. Removal of the solvent by rotary evaporation left a colorless liquid which was spectroscopically characterized as 2-cyclopropylbicyclo-[4.3.0]nona-1(9),2-diene (**5**). ^{1}H NMR: δ 5.78 (bm, 1 H), 5.44 (bm, 1 H), 2.66−2.54 (m, 1 H), 2.4−2.30 (m, 2 H), 2.16 (m, 3 H), 2.00−1.90 (m, 1 H), 1.51−1.30 (m,2H), 1.28−1.12 (m, 1 H, cyclopropyl H), 0.70−0.54 (m, 2 H), 0.49−0.40 (m, 1 H), 0.39−0.30 (m, 1 H). ^{13}C NMR: 144.67, 135.37, 123.10, 121.23, 44.03, 32.13, 31.55, 30.32, 26.42, 12.69, 5.84, 4.14. GC−MS: 160 (M^+, 52), 145 (11), 131 (52), 117 (100), 104 (22), 91 (91), 77 (23), 65 (20), 41 (28), 39 (33), 28 (100). HRMS for $C_{12}H_{16}$: calcd 160.1252, found 160.1252.

An NMR sample of diazene in benzene-d6 was degassed and sealed under vacuum. After the tube was heated in a water bath (100 °C) for 20 min, an ^{1}H NMR spectrum was recorded. Only hydrocarbon **5** was formed; dimers (see below) were not detected. An NMR sample of diazene **3** in deuteriochloroform was allowed to stand at room temperature for a week, and the NMR spectrum revealed the presence of only hydrocarbon **5**.

Photolysis of Diazene 3 at −78 °C. An NMR tube containing diazene (4 mg) and $CFCl_3$ (∼0.8 mL) (degassed and sealed) was photolyzed at −78 °C (dry ice/acetone) for 2.5 h with a Hanovia high-pressure mercury arc lamp using a Pyrex filter. An ^{1}H NMR spectrum was recorded in a precooled NMR probe (−80 °C) followed by a gradual increase in temperature up to −10 °C. The spectrum reveals few if any monomer resonances and consists mostly of dimers. MS of dimers: 320 (M^+, 3), 160 (47), 131 (17), 117 (28), 91 (24), 84 (100). HRMS

(12) Relative energies are difficult to compare here since intersystem crossing in TMM species is slow and results from a temperature-independent small transmission factor in transition state theory while cyclopropylcarbinyl ring-opening reactions have 7−8 kcal/mol enthalpic barriers so that the relative utilization of pathways is a strong function of temperature. Nonetheless, consideration of the fate of the *trans* allylcarbinyl species results in recognition that the transition state for ring opening of triplet TMM is higher than than for ring opening of singlet TMM.

(13) We thank Professor Paul Lahti for these calculations.

(14) Kerber, R. C.; Linde, H. G., Jr. *J. Org. Chem.* **1966**, *31*, 4321.

for $C_{24}H_{32}$: calcd 320.2504, found 320.2492. ^{1}H NMR (rel areas given): δ 5.70 (bm, 1.1); 5.64 (bm, 1.67); 5.56 (q, J = 4 Hz, 0.84); 3.0 (three multiplets, 6.41); 2.8 (bm, 2.18); 2.4−1.95 (m, 10.0); 1.95−1.65 (m, 5.70); 1.65−1.1 (m, 33.35); 1.0 (m) and 0.85 (m) ca. 1:1 (6.43 total rel area); 0.8 to −0.15 (m, 57.91).

Direct Photolysis of Diazene 3. Diazene **3** (8.6 mg) taken in an NMR tube containing benzene-d_6 (∼0.6 mL) was degassed and sealed by a torch. The NMR sample was photolyzed at 0−5 °C (ice/H_2O) for an hour by a Hanovia high-pressure mercury arc lamp using a Pyrex filter. In addition to monomer **5**, fused $C_{24}H_{32}$ dimers could be detected in the NMR judging by the presence of vinyl protons δ 5.70 (bm), δ 5.64 (bm), and δ 5.56 (quartet) in the ratio of 4:6:3. The ratio of monomer to dimers is ∼1:0.8. Further photolysis did not change the product compositions.

Effect of Concentration in the Direct Photolysis of 3. Two sealed tubes containing 5.0 and 5.7 mg of **3** and 0.7 mL and 1.5 mL of benzene, respectively, were photolyzed as described above. After photolysis the solvents were removed under aspirator vacuum, and the residues were analyzed by NMR. The ratios of monomer to dimer are 1:1 and 76:24, respectively, and are accurate to plus and minus 5%.

Photolysis of 3 in the Presence of Oxygen. A Pyrex tube containing diazene (5 mg) and cyclohexane (3.0 mL) at ∼0 °C was saturated with oxygen by bubbling oxygen gas through the solution by a 18 gauge needle. The solution was then photolyzed at 0−5 °C (ice/water) for 1.75 h. Removal of the solvent by rotary evaporation gave a residue which was identified by ^{1}H NMR as the 4,4-dicyclopropyl-2,3-dioxabicyclo-[3.3.0]oct-5-ene, **6**, (R_f = 0.5) along with a minor product (R_f = 0.8, see Results). Running the reaction on a larger scale followed by silica gel chromatography (CH_2Cl_2, eluent) did not afford any identifiable product other than the peroxide, **6**. ^{1}H NMR: δ 5.52 (td (5 lines), J = 3.6 and 1.6 Hz, 1H, 6-H), 5.30−5.25 (m (14 lines), 1H, 1-H), 2.94−2.82 (m, 1H, 7-H), 2.80−2.70 (m, 1H, 7-H), 2.17−2.10 (m, 1H, 8-H), 1.84−1.73 (m, 1H, 8-H), 1.19 (tt, J = 8.0 and 5.6 Hz, 1H, cyclopropyl H), 0.99 (tt, J = 8.0 and 5.6 Hz, 1H, cyclopropyl H), 0.70−0.22 (m, 8H, cyclopropyl H). HRMS for $C_{12}H_{16}O_2$: calcd 192.1150, found 192.1145

Sensitized Photolysis of Diazene 3 with an Argon Ion Laser. The contents of an NMR tube, 5 mg of diazene **3**, 2.5 mg of benzophenone, and 0.6 mL of benzene-d_6 (degassed and sealed), were photolyzed at 0−5 °C with the 364 nm line of an argon ion laser (CW) with the reaction being followed by NMR. After ∼3.5 h of photolysis almost all of the diazene decomposed, forming **5** and dimers mixture as was observed above (monomer : dimers = ∼1:0.8).

Electron Spin Resonance Experiments. Diazene **3** (∼20 mg) was placed in a 4 mm o.d. quartz ESR tube to which was added 100−130 μL of the appropriate solvent (2-methyltetrahydrofuran, 1- and 2-propanol mixture (2:3), propylene glycol). All solvents were distilled prior to use and were stored over molecular sieves. After degassing (three freeze−pump−thaw cycles) the tube was sealed. ESR spectra were obtained in a Bruker ESP-300 multiscan X-band spectrometer at 9.45 GHz field modulation frequency, 8.0 G modulation amplitude and 63−20 μW microwave power (for half-field absorptions higher power was used). ESR measurement at 77 K were carried out in frozen 2-methyl-THF solution with liquid nitrogen in a Suprasil finger dewar. The samples were photolyzed with a Photo Technology International 200 W Hg−Xe arc lamp in a housing with a parabolic reflector and a Pyrex water filter. The light was focused into the ESR cavity using a fiber optic light pipe. Typical photolysis times were 10−20 min. Variable temperature ESR measurements for photolysis were carried out in the ESP-300 spectrometer cavity equipped with a Bruker ER 4111 VT liquid nitrogen cryostat. Temperatures at the sample were calibrated with a carbon−glass thermocouple. ESR peak intensities were obtained as a function of temperature under identical scanning and microwave power conditions and then doubly integrated using Bruker ESP-300 software with the same integration endpoints for all specta of the sample obtained at various temperatures.

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