J. Am. Chem. Soc. **1982,** *104,* 2217–2222

Formal Kinetic Proof of Reversible Unimolecular Transformation to a Biradical as an Obligatory First Step in the Mechanism of Cycloaddition of 5-Isopropylidenebicyclo[2.1.0]pentane to Olefins[1]

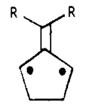
Mark R. Mazur[2] and Jerome A. Berson*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. *Received July 7, 1981*

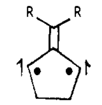
Abstract: A study of the kinetics of the cycloadditions of 5-isopropylidenebicyclo[2.1.0]pentane (**2b**) with acrylonitrile and maleic anhydride shows the operation of a two-step mechanism: unimolecular ring opening of the hydrocarbon to a singlet biradical (**1b-S**) followed by intermolecular capture of the singlet. The regiospecificity of the cycloaddition thus cannot be explained by a bimolecular hydrocarbon + olefin reaction [$_s2_\pi + {}_s2_\pi + {}_s2_\sigma$] but is most simply interpreted as an orbital symmetry effect dependent on the hierarchy of the nominally NBMOs of the diyl. The kinetic data permit the assignment of a barrier of about 2.3 kcal/mol to the cyclization of the singlet biradical.

The cycloaddition chemistry of 2-isopropylidenecyclopentane-1,3-diyl (**1b**) can be dissected into reactions of two molecular spin states, a singlet and a triplet.[3-5] The triplet species is clearly a biradical: it can be observed by electron paramagnetic resonance (EPR) spectroscopy, its reactions with olefins are stereorandom, and the order of triplet diylophilic reactivities of a series of olefins runs parallel to that of the same olefins in reactions with monoradicals. These findings suggest an intermediate (**1b-T**) with unpaired electronic spins which gives cycloadducts by two successive bond-forming steps.

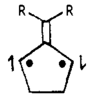
In contrast, the true nature of the singlet species has been difficult to determine. It has no EPR spectrum, its reactions with olefins are stereospecific, and the order of singlet diylophilic reactivities of a series of olefins runs parallel to that of the same olefins in Diels–Alder reactions with cyclopentadiene. These findings suggest an intermediate with paired electronic spins which gives cycloadducts by forming two bonds in a single concerted act, but they do not answer the question of whether the "singlet" is better represented as a bicyclic hydrocarbon (**2b**) or a true singlet biradical **1b-S**.



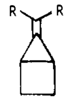
1



1-T



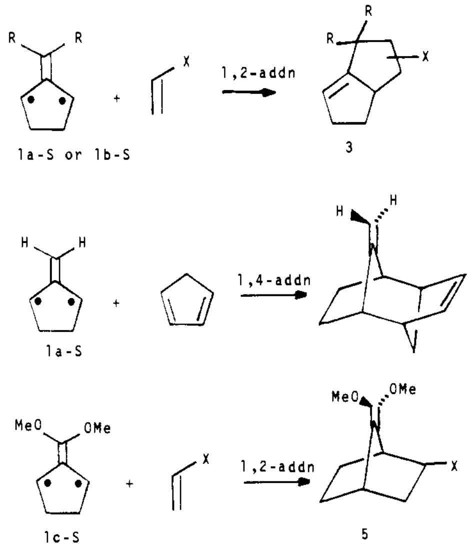
1-S

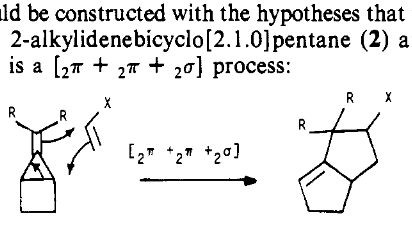


2

a: R = H
b: R = Me
c: R = OMe

Before the present[1] work, the most compelling argument in favor of the biradical **1b-S** (or a zwitterionic variant) was simply an appeal to mechanistic parsimony in rationalizing the regiospecificity of the singlet + olefin cycloaddition.[6] Thus, the reaction of **1a-S** or **1b-S** with an olefin (or the portion of the reaction with a conjugated diene that goes by 1,2 addition) gives predominantly *fused* product (e.g., **3**). This specificity switches to *bridged* product **4** in the 1,4 addition of a conjugated diene to **1a-S**, behavior that we attributed to the energy ordering of the nominally degenerate nonbonding molecular orbitals (NBMOS) of the planar singlet biradical (C_s symmetric below antisymmetric).[6] Similarly, the observed switch to regiospecific bridged product **5** in the 1,2 additions to the dimethoxy analogue **1c-S** found a ready explanation in terms of an electronic perturbation which tends to invert the order of the NBMOs.[7] Nevertheless, it was recognized that an alternative interpretation of the formation of regiospecific product could be constructed with the hypotheses that the reactive species is a 2-alkylidenebicyclo[2.1.0]pentane (**2**) and that cycloaddition is a [$_2\pi + {}_2\pi + {}_2\sigma$] process:





---

(1) Preliminary communication: M. R. Mazur and J. A. Berson *J. Am. Chem. Soc.* **1981**, *103*, 384.

(2) Humphrey Chemical Co. Fellow, 1981–.

(3) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446 and references cited therein.

(4) Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 276.

(5) Duncan, C. D.; Corwin, L. R.; Davis, J. H.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2350.

(6) (a) Siemionko, R.; Shaw, A.; O'Connell, G.; Little, R. D.; Carpenter, B. K.; Shen, L.; Berson, J. A. *Tetrahedron Lett.* **1978**, 3529. (b) Siemionko, R.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3870.

(7) Carpenter, B. K.; Little, R. D.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5723.

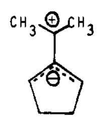
0002-7863/82/1504-2217$01.25/0

In the present paper, we take advantage of the recent synthesis[8a,b] of **2b**, a thermally labile but observable substance, to make a kinetically based identification of the biradical **1b-S** rather than the bicyclic hydrocarbon **2b** as the reactive species in the cycloadditions of the singlet with olefins.

Thermal unimolecular decomposition of hydrocarbon **2b** in acetone-d_6 solvent in the absence of a trapping olefin can be followed by nuclear magnetic resonance (NMR) spectroscopy at 270 MHz. The reaction occurs with clean first-order kinetics and gives the previously reported[3] dimers of **1**. The temperature dependence of the first-order rate constant, measured at eight points between −58 and −26 °C, gives the Arrhenius parameters $E_a = 13.7$ kcal/mol and log $A = 9.6$ (A in s^{-1}). These values are essentially the same as those obtained earlier,[8a,b] $E_a = 13.3$ and 13.6 kcal/mol and log $A = 9.2$ and 9.6, for reactions in two different solvent systems, $CDCl_3$–$CFCl_3$ and $CDCl_3$–CCl_4, respectively.

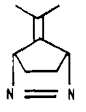
The Arrhenius A factor is only about 10^{-4}–10^{-5} as large as might have been expected[9a] for a thermal unimolecular decomposition. We have previously interpreted this in terms of a spin-forbidden transition state, in which intersystem crossing from the singlet to the triplet manifold occurs. The triplet biradicals so formed then dimerize.[8a,b]

Although we have discussed several points in favor of this mechanism,[8a,b] spin-forbidden thermal reactions are so rare[8c] that it seems wise to consider other possible explanations for the low A factor. One such alternative might be constructed around the hypothesis that the rate-determining step in the thermal decomposition of **2b** is the formation of a zwitterionic intermediate, e.g., **6**. The strongly dipolar nature of such a species would cause an electrostriction of solvent molecules in the vicinity, which could cause a substantial negative contribution to the entropy of the transition state.[9b] Solvent polarity then should have a strong effect on the rate. If we assume that the solvent polarity parameter E_T[10] for $CDCl_3$–$CFCl_3$ is the average (36 kcal/mol) of those for the two pure components, a change to acetone, $E_T = 42$ kcal/mol, represents a modest increase in solvent polarity without a discernible effect on the rate or activation parameters. Moreover, electrostriction effects are likely to involve specific solvation rather than the blend of properties included under "polarity". There is no obvious reason why these should remain constant through the solvents examined. No explicative purpose would be served by the addition of subsidiary hypotheses to bolster the zwitterionic mechanism for the unimolecular decomposition of **2b**.



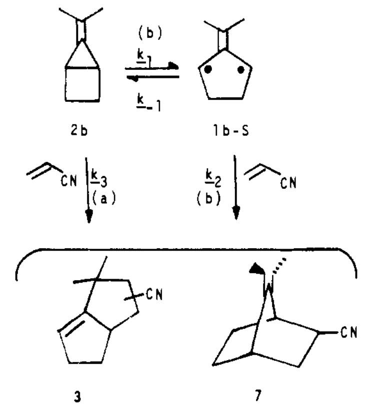
6

Kinetics of Cycloaddition. Incorporation of a large excess of a conjugated olefin such as acrylonitrile into the reaction mixture increases the rate of disappearance of **2b**. The product is the same mixture of cycloadducts, **3** and **7**, as is obtained upon capture of the singlet species when it is generated by deazetation of diazene **8** in acrylonitrile (Scheme I).[3-5] Fused adducts (**3**) are the major products in both instances.



8

Scheme I



Two hypothetical mechanisms (Scheme I) which predict different kinetic behavior can be considered as pathways for the formation of cycloadducts **3** and **7** from hydrocarbon **2b**: (a) Direct bimolecular collision of **2b** with the olefin would result in second-order kinetics. (b) Reversible unimolecular interconversion of **2b** and some reactive intermediate, conveniently formulated as a singlet biradical **1b-S**, predicts first-order kinetics when the ring-opening step is rate determining, second-order kinetics when the capture step is rate determining, and intermediate behavior when the rate determining step is not well defined. Note that a mechanism involving *irreversible* formation of the intermediate **2b** → **1b-S** followed by bimolecular capture of **1b-S** (**1b-S** + olefin → products) would display first-order kinetics. A mechanism involving the reversible change **2b** ⇌ **1b-S** as a side reaction in competition with bimolecular capture of hydrocarbon **2b** would lead to second-order kinetics and would be indistinguishable from mechanism a by the present technique.

Under the pseudo-first-order conditions of the present experiments, mechanism a predicts a linear response of the pseudo-first-order rate constant, k_{obsd}, to the acrylonitrile concentration, [M]. The steady-state approximation applied to mechanism b predicts the relationship of eq 1, which may be converted to linear form as its reciprocal, eq 2. Exclusive operation of mechanism

$$k_{obsd} = k_1k_2[M]/(k_{-1} + k_2[M]) \qquad (1)$$

$$1/k_{obsd} = (k_{-1}/k_1k_2[M]) + 1/k_1 \qquad (2)$$

b thus would lead to a linear plot of $1/k_{obsd}$ vs. $1/[M]$ with a finite intercept, $1/k_1$. The double-reciprocal plot also would be linear for mechanism a (bimolecular collision), but as eq 3 shows, it would have a zero intercept.

$$1/k_{obsd} = 1/k_3[M] \qquad (3)$$

The reaction of **2b** with a 10-fold excess of acrylonitrile at −55 °C in acetone-d_6 can be followed by the same kinetic technique described for the dimerization of **2b**. A double-reciprocal plot of the data (Figure 1A) is linear with an intercept of 1.186×10^3 s. As is shown elsewhere,[1] a Scatchard plot[11] (k_{obsd} vs. $k_{obsd}/[M]$) of the same data, which should emphasize any curvature masked by the double-reciprocal plot, also is linear.

The observation of a linear double-reciprocal dependence and a finite intercept are consistent with the exclusive operation of two-step mechanism b. The diylophilic reactivity of acrylonitrile evidently is in an intermediate range, since neither the first-order nor the second-order extreme of behavior predicted by mechanism b is observed.

In mechanism b, the intercept of the double-reciprocal plot is the reciprocal of k_1, the unimolecular rate constant for ring opening. The trapping agent is not involved in this step, and accordingly, all trapping agents should give the same intercept. Moreover, the first term of eq 2 becomes small relative to $1/k_1$ if $k_2[M]$ greatly exceeds k_{-1}, that is, when bimolecular trapping of the intermediate **1b-S** is much faster than recyclization. Thus,

---

(8) (a) Rule, M.; Lazzara, M. G.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7091. (b) Rule, M.; Mondo, J. A.; Berson, J. A. *Ibid.* **1982**, *104*, 2209. (c) For a list of references to discussions of these processes, see ref 8b, footnote 26.

(9) (a) Frost, A. A.; Pearson, R. J. "Kinetics and Mechanism"; Wiley: New York, 1953, Chapter 4. (b) Reference 9a, p 130; (c) Reference 9a, p 318.

(10) Kosower, E. M. "Physical Organic Chemistry"; Wiley: New York, 1968; p 293.

(11) Scatchard, G. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 660.

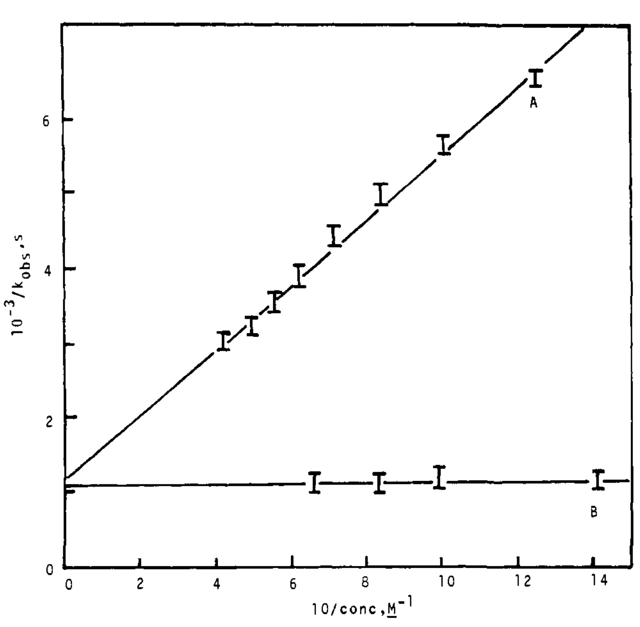


Figure 1. Dependence of the reciprocal of the pseudo-first-order rate constant, k_{obsd}, on the reciprocal of the concentration of the trapping agent acrylonitrile (A) or maleic anhydride (B) in the reaction with 5-isopropylidenebicyclo[2.1.0]pentane (**2b**) at −55 °C in accetone-d_6 solvent.

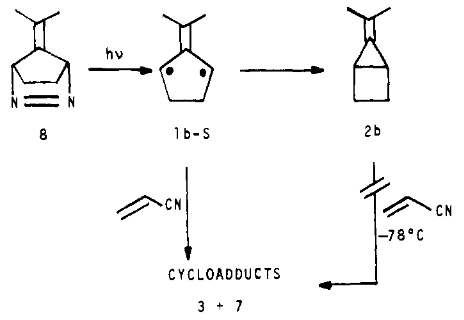
a high concentration of a very reactive trapping agent should give a double-reciprocal plot with the same intercept seen for acrylonitrile but with a near-zero slope.

Previous direct competition studies[3,5] have shown that at 60 °C, maleic anhydride is 52 times as reactive as acrylonitrile toward the singlet. If this preference persists or increases at the temperature of the present experiments (−55 °C), a change to the first-order extreme of mechanism b with maleic anhydride might be expected. Indeed, Figure 1B shows that the pseudo-first-order rate constant is virtually insensitive to the concentration of maleic anhydride in the experimental range. This invariant behavior is characteristic of mechanism b when the rate-determining step is unimolecular formation of the reactive intermediate (**2b** → **1b-S**).

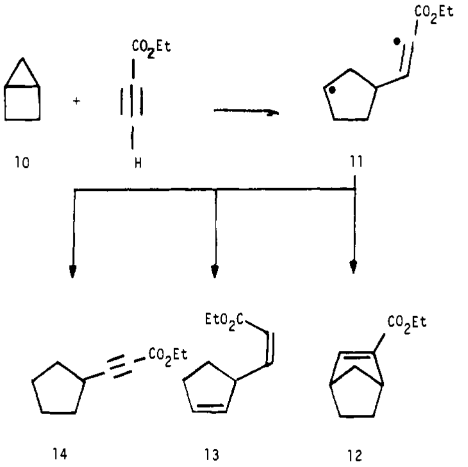
As required by mechanism b, the intercepts of the acrylonitrile and maleic anhydride plots are identical within experimental error. From the intercepts, the values 8.43 and 9.06 × 10^{-4} s^{-1} can be obtained for k_1, the rate constant for the unimolecular ring-opening step. The slope and intercept of Figure 1A, inserted into eq 2, permit the calculation $k_{-1}/k_2 = 3.7$ M, the ratio of rate constants for intramolecular cyclization and intermolecular capture of the species **1b-S** by acrylonitrile.

Intermolecular Capture of Photochemically Generated 1b-S. Mechanism b treats the singlet biradical **1b-S** kinetically as a local minimum in a potential-energy surface, not as a transition state. The same species has been implicated in the photolytic deazetation of the diazene **8**.[8a,b] This suggests that if the photodeazetation is carried out in the presence of a high concentration of trapping agent, it might be possible to intercept **1b-S** before if cyclizes to **2b**. We now find that photolysis of **8** in the presence of 2 M acrylonitrile in acetone-d_6 at −78 °C gives a mixture of 80% of hydrocarbon **2b** and 20% of cycloadducts **3** and **7**, with **3** predominant (Scheme II). The same experiment with 1.0 M maleic anhydride instead of acrylonitrile gives <5% of **2b** and >95% of the analogous cycloadducts. In neither experiment can the formation of the cycloadducts be a simple thermal reaction of photochemically generated hydrocarbon **2b** with the trapping olefin, since control experiments show that process to be immeasurably slow at −78 °C. The results are most simply formulated (Scheme II) in terms of a competition between intramolecular ring closure and bimolecular capture of an intermediate. As would be expected, the relative importance of the capture reaction increases with the diylophilic reactivity of the trapping agent.

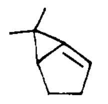
Scheme II



Scheme III



The results indicate the formation of a discrete, trappable intermediate in the thermolysis of hydrocarbon **2b**, and in the photolysis (and thermolysis[3-5]) of diazene **8**. This species cannot be a bicyclo[3.1.0]hex-1-ene (**9**), since derivatives of this ring



9

system behave in an entirely different manner[12,13] and since the switches in regiospecificity of cycloaddition[6] find no clear interpretation in such a hypothesis. Nor can the triplet **1b-T** be the intermediate, since its chemistry is also different.[3-5] It is difficult to propose candidates other than **1b-S** for the role of the singlet species, the identification of which now brings to a total of four (**1b-S**, **1b-T**, **2b**, and **9**) the explicitly recognizable entities of the 2-isopropylidenecyclopentane-1,3-diyl family.

Discussion

Mechanistic Comparison of the Addition Reactions of Bicyclopentane and Its 5-Isopropylidene Derivative. Previous studies[14,15] have developed a mechanism for the addition reactions of strained bicyclic compounds with olefins and acetylenes that differs significantly from the two-step unimolecular-then-bimolecular sequence (mechanism b, Scheme I) deduced here for the cycloadditions of **2b**. In the addition of ethyl propiolate to bicyclo[2.1.0]pentane (**10**), for example, the proposed[14] mechanism in-

---

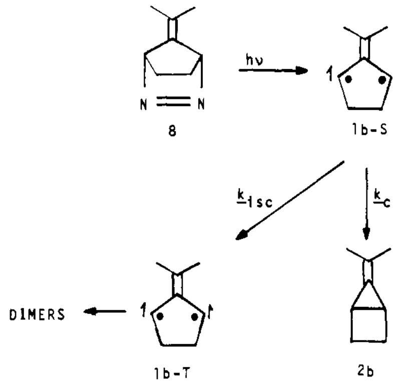
[12] (a) Köbrich, G.; Heinemann, H. *Chem. Commun.* **1969**, 493. (b) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 464.

[13] (a) Rule, M.; Berson, J. A. *Tetrahedron Lett.* **1978**, 3191. (b) Rule, M.; Salinaro, R. F.; Pratt, D. R.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2223. (c) Salinaro, R. F.; Berson, J. A. *J. Am. Chem. Soc.*, **1979**, *101*, 7094. (d) Salinaro, R. F.; Berson, J. A. *ibid.* **1982**, *104*, 2228.

[14] (a) Gassman, P. G.; Mansfield, K. T. *Chem. Commun.* **1965**, 391. (b) Gassman, P. G.; Mansfield, K. T. *J. Am. Chem. Soc.* **1968**, *90*, 1517. (c) Gassman, P. G.; Mansfield, K. T.; Murphy, T. J. *Ibid.* **1968**, *90*, 4746. (d) Gassman, P. G.; Mansfield, K. T.; Murphy, T. J. *Ibid.* **1969**, *91*, 1684. (e) Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128.

[15] Cairncross, A.; Blanchard, E. P., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 496.

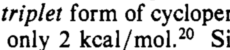
Scheme IV



volves a bimolecular-then-unimolecular pathway, initiated by the rate-determining formation of an *adduct* biradical **11**. This species can cyclize to give product **12** or undergo hydrogen shift to give products **13** or **14** (Scheme III). (We have not found analogous hydrogen-shifted products in the reactions of **2b**.) In accord with the mechanism of Scheme III, the observed kinetics are overall *second order* (first order in each component, the trapping agent and the strained hydrocarbon).[14] Moreover, the reactions of **10** with maleonitrile and fumaronitrile do not preserve stereochemistry,[14] in contrast to those of olefins with **1b-S** derived from diazene **8**, which are highly stereospecific.[3-5]

Evidently, the addition reactions of bicyclopentane (**10**) and its 5-isopropylidene derivative (**2b**) proceed by different pathways. Whether structurally altered 5-alkylidenebicyclopentanes can be diverted into the bimolecular-then-unimolecular mechanism of Scheme III, or into some other mechanism of cycloaddition, remains to be elucidated.[16]

On the Energy Barrier to Cyclization of the Singlet Biradical 1b-S. The barrier to ring closure of singlet 1,3-biradicals remains a controversial subject.[17] In the case of trimethylene (**15**), for

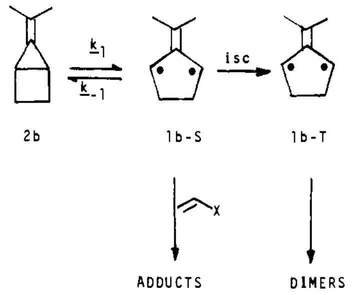


15

example, a comparison of the heat of formation (ΔH_f°) of **15** calculated from bond-additivity tables with ΔH_f° of the transition state for stereomutation of 1,2-dideuteriocyclopropane places a barrier of about 9 kcal/mol between the biradical and the cyclic hydrocarbon.[18] On the other hand, the best available quantum-mechanical-energy surface[19] shows no local minimum on the singlet stereomutation pathway. Even the increased strain of the bicyclopentane system **10** does not produce a substantial barrier. Ring closure of the *triplet* form of cyclopentane-1,3-diyl (**16**) to **10** has a barrier of only 2 kcal/mol.[20] Since the triplet is the ground state of this biradical,[20] the barrier to cyclization of the singlet probably is smaller than 2 kcal/mol.

16 10

Scheme V



We can estimate the ring-closure barrier in **1b-S** in several ways. The first takes advantage of the observed[8a,b] temperature dependence of the product composition in the photolysis of the diazene **8**, which is caused by a competition between cyclization (rate constant k_c) and intersystem crossing (k_{isc}) in the intermediate biradical **1b-S** (Scheme IV). The intersystem crossing rate constant can be used as an internal clock against which to measure k_c. Thus, the ratio k_c/k_{isc}, given by the ratio of products **2b**:dimers, is >19 at −78 °C in solution and 0.3 when a glassy matrix containing **8** is irradiated at −196 °C and then melted. If we disregard the change in medium, the temperature dependence corresponds to a difference in activation energy $E_c - E_{isc}$ of about 1.05 kcal/mol. The barrier for isc is less than 0.27 kcal/mol, as estimated by the rise time of <1 ms for appearance of the EPR signal upon flash photolysis of **8** at 4.2 K.[21] Thus, 1.3 kcal/mol represents a crude lower limit of the activation barrier for ring closure.

In fact, the barrier must be somewhat higher than this to permit intermolecular capture of **1b-S** if the diffusion-controlled encounter frequency is taken as the upper limit for the trapping rate. In acetone at −78 °C at 1 M maleic anhydride, this would be about $3 \times 10^9\ \mathrm{s^{-1}}$, whereas k_c would be about $3.6 \times 10^{10}\ \mathrm{s^{-1}}$ (assuming an Arrhenius A factor of $10^{12}\ \mathrm{s^{-1}}$) if E_c were as small as 1.3 kcal/mol. A barrier $E_c \simeq 2.3$ kcal/mol would be required to achieve approximate equivalence of the trapping and ring-closure rates. Since this calculation depends crucially upon the A-factor estimate, for which no experimental precedent exists, it must be considered speculative.

Another estimate of E_c ($\equiv \Delta H_c^\ddagger + RT$) can be obtained from the kinetic data on the thermal dimerization and cycloaddition reactions of **2b**. The simplest formulation of dimerization in the absence of a trapping agent would involve a sequence **2b** $\rightleftharpoons$ **1b-S** → **1b-T** → dimers, with the actual rate-determing step being **1b-S** → **1b-T** (Scheme V). This accounts for the observed first-order kinetics and the low A factor. It is merely an expanded version of Scheme I, with the added feature that isc and dimerization now are explicitly included. The singlet biradical **1b-S** is a common intermediate on both pathways, one leading to adducts and the other to dimers. Since the activation energy for isc presumably cannot be negative, it would seem to follow that the energy of the transition state for dimerization must be at least as great as that for formation of the singlet intermediate **1b-S**. At −55 °C, the activation energy ($\Delta H_{II}^\ddagger = E_{II} - RT$) for the thermal dimerization of **2** in acetone-d_6 is 13.3 kcal/mol. We can estimate the activation energy ($\Delta H_I^\ddagger$) for formation of **1b-S** from the value of k_1, $8.75 \times 10^{-4}\ \mathrm{s^{-1}}$, determined from the intercept of the double-reciprocal plot (Figure 1). This corresponds to $\Delta G_I^\ddagger = 15.6$ kcal/mol. Since $\Delta S_I^\ddagger$ would be expected to be zero or positive for this reaction,[9,18] $\Delta H_I^\ddagger \geq 15.6$ kcal/mol.

Superficially, this seems to argue against the common intermediacy of **1b-S** and in favor of two separate pathways. However, the discrepancy $\Delta H_I^\ddagger > \Delta H_{II}^\ddagger$ is only apparent, and a "reversed" inequality is exactly what would be expected if Scheme V prevailed. This can be grasped qualitatively by noting that the **2b** → **1b-S** ring-opening reaction is reversible and that the barrier to ring closure of **1b-S** is finite and larger than that for isc. Thus, an increase of temperature will send a greater fraction of the **1b-S** intermediate back to **2b**. In these circumstances, the measured *apparent* activation energy for the ring-opening step, $\Delta H_I^\ddagger$, will

---

(16) A change in mechanism may be involved in the addition reactions of 1-*tert*-butyl-5-isopropylidenebicyclo[2.1.0]pentane: Salinaro, R. F.; Berson, J. A. unpublished work.

(17) For reviews, see: (a) Berson, J. A. *Annu. Rev. Phys. Chem.* **1977**, *28*, 111. (b) Berson, J. A. In "Rearrangements in Ground and Excited States", P. de Mayo, Ed.; Academic: New York, 1980; Vol. I, p 324. (c) Bergman, R. G. In "Free Radicals", Kochi, J., Ed.; Wiley: New York, 1973; Vol. I, p 191. (d) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (e) Berson, J. A.; Pedersen, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1976**, *98*, 122.

(18) (a) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 83. (b) Benson, S. W. *J. Chem. Phys.* **1961**, *34*, 521. (c) O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866.

(19) Horsley, J. A.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R. S.; Wright, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 279.

(20) Buchwalter, S.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857; **1979**, *101*, 4688.

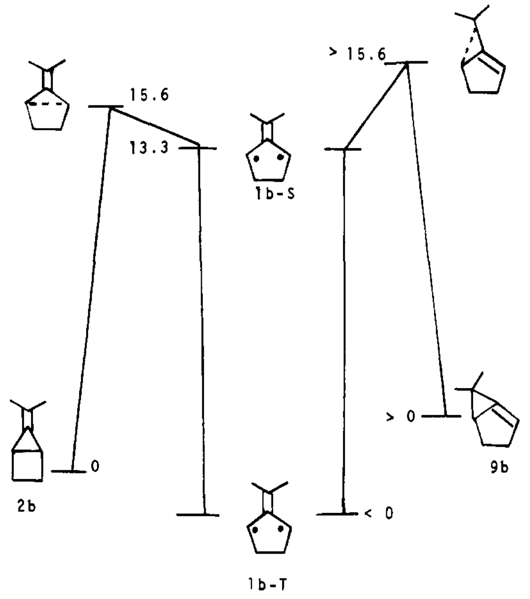


Figure 2. Energy surface connecting the bicyclic hydrocarbons **2b** and **9b** with the singlet (**1b-S**) and triplet (**1b-T**) diyls. Compound **2b** is arbitrarily assigned an energy of 0 kcal/mol. The energy separations **9b**-**2b**[13] and **2b**-**1b-T**[8] are shown qualitatively. The transition state between **1b-S** and **9b** is placed higher than that between **1b-S** and **2b** because the photolysis of diazene **8**, which passes through **1b-S** as an intermediate, gives **2b** rather than **9b**.[8] Triplet diyl **1b-T** probably is the global minimum.[8] The bisected singlet biradical, which may well be on the pathway to **9b**, is not shown.

be greater than that for the dimer-forming pyrolysis of **2b**. In fact, it can be shown (see Appendix) that the *difference* in the two activation energies, $\Delta H_{\text{I}}^{\ddagger} - \Delta H_{\text{II}}^{\ddagger} = 2.3$ kcal/mol, is approximately equal to the activation energy for ring closure, $\Delta H_{\text{c}}^{\ddagger}$. Experimental uncertainties in both $\Delta H_{\text{I}}^{\ddagger}$ and $\Delta H_{\text{II}}^{\ddagger}$ make it necessary to treat the numerical value of their difference with some skepticism. Moreover, the possibility of a quantum-mechanical tunneling contribution to the ring-closure rate, similar to that observed in the analogous case of cyclopentane-1,3-diyl,[20] must be considered. Nevertheless, the important point is that the sign and magnitude are consistent with the existence of a small but finite ring-closure barrier.

The Energy Surface. Figure 2 shows the energy relationships among the four local minima and two transition states of the 2-isopropylidenecyclopentane-1,3-diyl family. Direct observation and/or intermolecular capture evidence now has been provided for each of the local minima. The energy separation between the singlet and triplet biradicals, ≥13.3 kcal/mol, is in poor agreement with our previously reported value[22] of <3.5 kcal/mol, which was based upon the assumption that the (then unknown) bicyclic compound **2b** did not serve as a source of singlet product in molten matrix trapping experiments. With the assumption now having been invalidated,[8a,b] the earlier results[22] cannot be directly translated into an energy separation without further work.[23] Although the effect of methyl-for-hydrogen substitution is unknown, the value ≥13.3 kcal/mol (Figure 2) is not incompatible with the most recent theoretical calculations[24] on 2-methylenecyclopentane-1,3-diyl (**1a**), which show a triplet-*planar* singlet energy gap of 18.7 kcal/mol.

The same calculation[24] predicts that the triplet diyl **1a-T** should be 10.3 kcal/mol more stable than the corresponding 2-methylenebicyclopentane (**2a**). This is in good agreement with the experimentally based suggestion[8a,b] that the triplet biradical **1b-T** is more stable than hydrocarbons **2b** and **9b**.

On the Regiospecificity of the Singlet Cycloadditions. The present work rules out any explanation of the observed regiospecificity[3-5] of the singlet cycloadditions of **2b** in terms of direct $[{}_s2_\pi + {}_s2_\pi + {}_s2_\sigma]$ reaction of the bicyclic hydrocarbon with the olefin. A more general explanation[6] based on the frontier MO properties of the biradical **1b-S** clearly is preferred. The regiospecificities imply a planar configuration for the *reactive* form of **1b-S**, but it seems likely that the *bisected* species is readily accessible, as is predicted theoretically[24] for the analogue **1a-S** and observed experimentally[25] for 4-methoxy-2-methylenecyclopentane-1,3-diyl.

Conclusions. Cyclization of the resonance stabilized singlet biradical **1b-S** to the strained hydrocarbon **2b**, which is weakly exothermic (by 13.3 kcal/mol), requires an activation barrier of only about 2 kcal/mol (Figure 2). In contrast, the cyclization of the simple, unstabilized trimethylene biradical **15** to cyclopropane has been postulated by bond additivity methods to be strongly exothermic (by 56 kcal/mol) and yet has been assigned a much higher barrier, 9 kcal/mol.[18] Physical reasons may exist for these apparently incompatible relationships. Until these are brought to light, however, it seems prudent to consider the alternative viewpoint[17,19,20] that the barriers to ring closure in singlet 1,3-biradicals are very low.

As far as we know, the present work records the first example of an operationally detectable singlet hydrocarbon biradical. At room temperature, the ring-closure barrier of about 2 kcal/mol and the *A* factor of about $10^{9.5}$ for isc should result in unimolecular half-lifetimes of about 10^{-11} s and 10^{-10} s, respectively, for the two processes. It must be stated that chemical interception and kinetic analysis, the methods used for its identification, are indirect, and spectroscopic observation would be most desirable. Given the favorable spectroscopic properties predicted for the biradical,[26] modern fast kinetic techniques[27] should be capable of achieving this goal.

Experimental Section

Kinetic operations were carried out by the techniques described elsewhere.[8b] Temperatures in the probe of the Bruker 270 MHz NMR spectrometer were measured to ±0.2 K by the difference in chemical shift of the CH_3 and OH resonances of a methanol standard. No variation was observed during a run, but day-to-day changes in operating conditions could cause as much as 1.5 K difference between two nominally identical temperature settings. Therefore, eq 4 was used to make small

$$\ln k_{\text{obsd}} = (\ln k' - 32)\frac{T_{\text{obsd}}}{218.1} + 32 \qquad (4)$$

corrections to adjust all of the cycloaddition rate determinations to a common temperture of −55 °C (218.1 K). The *A* factor was assumed to be $\sim 10^{14}$ s^{-1} ($\ln A \sim 32$). The raw rate constant k' was defined as $k' = (1/t) \ln (I_0/I)$, where I_0 and I refer to the initial and timed integrated intensities of the methyl resonance of **2b**.

Rates of Reaction of 2b with Olefins. Acrylonitrile. From a microliter syringe, 100 μL of a stock solution (340.5 mg in 5 mL of acetone-d_6) of the diazene **8** was transferred into an NMR tube. To this was added an appropriate amount of an acrylonitrile stock solution (1.0 mL of acrylonitrile in 5 mL of acetone-d_6). The volume was brought to 500 μL with acetone-d_6. The tube was degassed by a freeze-pump-thaw cycle and sealed under vacuum.

This sample was placed in a transparent Dewar flask and photolyzed at 3500 Å for 2 h at −78 °C in a Rayonet reactor. The proton probe of the Bruker HX-270 NMR spectrometer was cooled to 218.1 K, the sample was quickly placed into the probe, and the spectrum was scanned every 5 min.

Control experiments showed that **2b** did not react with acrylonitrile at −78 °C. Yet when one of the above irradiation mixtures (2 M acrylonitrile) was examined in the NMR spectrometer at −78 °C, the product consisted of 80% of **2b** and 20% of the same cycloadducts as were formed[3-5] when diazene **8** was photolyzed in the presence of acrylonitrile.

---

[21] Platz, M. S.; Kelsey, D. R.; Berson, J. A.; Turro, N. J.; Mirbach, M. *J. Am. Chem. Soc.* **1977**, *99*, 2009.

[22] Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5178.

[23] For further discussion, see: Berson, J. A. In "Diradicals", Borden, W. T., Ed.; Wiley: New York, 1982.

[24] Dixon, D. A.; Dunning, T. H., Jr.; Eades, R. H.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878.

[25] (a) Lazzara, M. G.; Harrison, J. J.; Rule, M.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7092. (b) Lazzara, M. G.; Harrison, J. J.; Rule, M.; Hilinski, E. F.; Berson, J. A. *Ibid.* **1982**, *104*, 2233.

[26] Cf.: Davis, J. H.; Goddard, W. A., III *J. Am. Chem. Soc.* **1977**, *99*, 4242.

[27] Rentzepis, P. M. *Adv. Chem. Phys.* **1973**, *23*, 189.

Table I. Thermal Decomposition of 2b in the Presence of Olefins

concn, M	$k' \times 10^4$s	temp, K	$k_{obsd} \times 10^4$s	av $k_{obsd} \times 10^4$s
acrylonitrile				
0.8	1.754	218.9	1.511	1.529
	1.547	218.1	1.547	
1.0	1.887	218.5	1.752	1.757
	2.433	218.8	2.137	
	1.843	218.4	1.743	
	2.062	218.9	1.778	
1.2	1.801	217.5	2.014	2.019
	2.025	218.1	2.025	
1.4	2.113	217.5	2.362	2.274
	2.359	218.3	2.274	
	1.938	217.5	2.167	
	2.378	218.3	2.292	
1.6	2.608	218.3	2.513	2.569
	3.040	218.9	2.624	
1.8	2.626	217.8	2.775	2.794
	2.677	217.8	2.829	
	2.828	218.2	2.777	
2.0	3.155	218.3	3.041	3.041
2.4	3.419	218.3	3.296	3.296
maleic anhydride				
0.7	9.866	219.1	8.253	8.253
1.0	11.380	219.9	8.263	8.267
	8.481	218.3	8.183	
	8.362	218.1	8.362	
1.2	10.953	219.5	8.538	8.538
1.5	8.267	217.8	8.724	8.724

When the experiment was repeated at 1.0 M acrylonitrile concentration, the product consisted of ~95% of **2b** and 5% of cycloadducts.

Maleic Anhydride. Photolysis of diazene **8** in the presence of maleic anhydride at −78 °C gave mostly (>95%) cycloadducts and <5% of **2b**. Again, **2b** and maleic anhydride did not react at −78 °C. Therefore, a different technique was used in these runs. A sample of 100 μL of the above diazene stock solution was transferred by syringe to an NMR tube, and to this was added enough acetone-d_6 to make a total volume of 500 μL when the maleic anhydride stock solution (978 mg in 5 mL of acetone-d_6) was added. The tube was capped with a rubber septum, fitted with a hypodermic needle, degassed by a freeze–jump–thaw cycle, and filled with nitrogen.

The sample was photolyzed for 2 h at −78 °C and frozen in liquid nitrogen, and the maleic anhydride solution was transferred in by syringe. After having been transferred to a bath held at −60 to −65 °C and shaken vigorously to ensure that all of the maleic anhydride was in solution, the sample was treated in the same way as the acrylonitrile sample.

The individual kinetic runs were pseudo first order with correlation coefficients >0.999 in most cases. The data are presented in Table I in uncorrected form (k') and after adjustment (k_{obsd}) and plotted in Figure 1. Although the stock solutions were made up at 25 °C and the kinetic runs were carried out at −55 °C, no attempt was made to correct the reagent concentrations for the temperature difference.

Acknowledgment. The support of this work by the Humphrey Chemical Co., the National Science Foundation (CHE 8011399), and the National Institute of General Medical Sciences (GM 23375) is gratefully acknowledged. We also think the National Science Foundation for its support of the NSF Regional NMR Facility at Yale University (CHE 7916210) and Professor D. A. Dixon (University of Minnesota) for an advance copy of his manuscript (ref 24).

Appendix

The relationship between the apparent Arrhenius activation energy, E_r, for the thermal dimerization of **2b** and the activation energies for the individual mechanistic steps can be derived by an adaptation of a discussion given for another case.[9c] With reference to Scheme V, we let k_{isc} be the rate constant for conversion of the singlet intermediate **1b**-S to dimers. The overall rate constant for disappearance of **2b**, k_r, can be expressed as

$$k_r = \frac{k_1 k_{isc}}{k_{-1} + k_{isc}} \tag{5}$$

by the Van't Hoff relation

$$\frac{d \ln k_r}{dT} = \frac{d}{dT} \ln \frac{k_1 k_{isc}}{k_{-1} + k_{isc}} = \frac{E_r}{RT^2} \tag{6}$$

Separating terms we obtain

$$E_r = E_1 + E_{isc} - \frac{k_{-1}E_{-1}}{k_{-1} + k_{isc}} - \frac{k_{isc}E_{isc}}{k_{-1} + k_{isc}} \tag{7}$$

By definition,

$$\frac{k_{-1}}{k_{-1} + k_{isc}} = \frac{A_{-1}e^{-E_{-1}/RT}}{A_{-1}e^{-E_{-1}/RT} + A_{isc}e^{-E_{isc}/RT}} = \frac{1}{1 + \dfrac{A_{isc}}{A_{-1}}e^{(E_{-1}-E_{isc})/RT}}$$

$$\frac{k_{isc}}{k_{-1} + k_{isc}} = \frac{1}{1 + \dfrac{A_{-1}}{A_{isc}}e^{(E_{isc}-E_{-1})/RT}}$$

If $E_{isc} \sim 0$ (see text) and if $A_{isc} \sim 10^{-4}A_{-1}$ (isc is spin forbidden), eq 7 becomes

$$E_r \simeq E_1 - E_{-1} \tag{8}$$

In other words, the apparent activation energy for dimer formation is *smaller* than that for ring opening by an amount equal to the activation barrier for ring closure.

Registry No. 1b, 32553-01-8; **2b**, 72447-89-3; **3**, 80939-31-7; **7**, 80954-13-8; **8**, 31689-32-4; **9b**, 80954-14-9; acrylonitrile, 107-13-1; maleic anhydride, 108-31-6.