Are Perpendicular Alkene Triplets Just 1,2-Biradicals? Studies with the Cyclopropylcarbinyl Clock†

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Received May 11, 1992. Revised Manuscript Received December 30, 1993®

Abstract: Thermochemical studies of perpendicular alkene triplets demonstrate that their energies are almost exactly those expected from Benson estimations using group equivalents for appropriate free radicals as models for the termini (the two essential carbons of the alkene triplet). If these species are to be described as 1,2-biradicals, their reactivities in reactions for which the termini act independently should be similar to corresponding reactivities for appropriate free-radical models. We have used the "cyclopropylcarbinyl clock", the rearrangement of a cyclopropylcarbinyl radical to the corresponding homoallyl radical, to test such a model. We have synthesized *cis-* and *trans-β*-cyclopropylstyrene (***cis*-1** and ***trans*-1**), α-cyclopropylstyrene (**2**), α-cyclopropylindene (**3**), and β-cyclopropylindene (**4**). We have studied their triplet chemistry and have examined the transients produced upon triplet sensitization by nanosecond laser flash photolysis. The results are consistent with two basic hypotheses: (1) that, when able to access the perpendicular configuration, cyclopropylcarbinyl ring opening occurs at the rate expected from an appropriate monoradical model and (2) that, when constrained in a higher energy (near-planar) geometry, the rate of ring opening is accelerated.

Much effort has been directed toward a fundamental understanding of alkene triplets and triplet biradical energetics, conformations, dynamics, and ultimately their roles in determining the outcomes of photochemical reactions.[1] Unconjugated alkene triplets are likely to be twisted at equilibrium to the well-known perpendicular structure[2,3] which is shown in Figure 1. Thermochemical studies of perpendicular alkene triplets[4] demonstrate that their energies are almost exactly those expected from Benson estimations[5] using group equivalents for appropriate free radicals as models for the termini (the two essential carbons of the alkene triplet). This suggests that the perpendicular orbitals interact negligibly, leading to description as a "1,2-biradical". For perpendicular triplets, free-radical-like chemistry and reactivity might thus be observed. Reactivities in reactions for which the termini act independently should be similar to corresponding reactivities for appropriate free-radical models.

We have used the "cyclopropylcarbinyl clock", the rearrangement of a cyclopropylcarbinyl radical to the corresponding homoallyl radical,[6–9] to test such a model. Since Bonneau[10] and Caldwell and Cao[11,12] have reported that the triplet states of acyclic styrenes are twisted to a perpendicular geometry when relaxed, we chose to study cyclopropyl-substituted styrenes. We have synthesized *cis-* and *trans-β*-cyclopropylstyrene (***cis*-1** and ***trans*-1**), α-cyclopropylstyrene (**2**), α-cyclopropylindene (**3**), and β-cyclopropylindene (**4**). We have studied their triplet chemistry and have examined the transients produced upon triplet sensitization by nanosecond laser flash photolysis. The results are consistent with two basic hypotheses: (1) that, when able to access the perpendicular configuration, cyclopropylcarbinyl ring opening occurs at the rate expected from an appropriate monoradical model and (2) that, when constrained in a higher energy (near-planar) geometry, the rate of ring opening is accelerated.

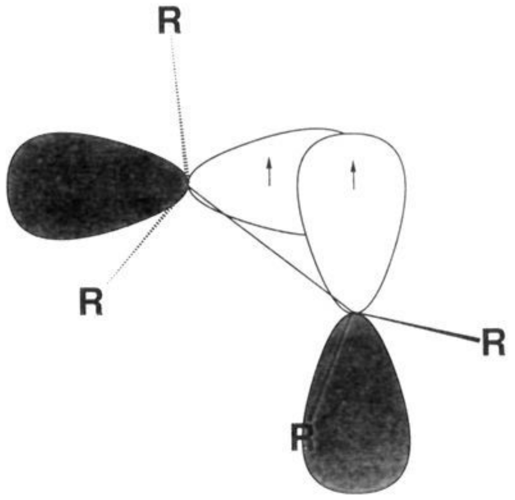

Figure 1. Sketch of a perpendicular alkene triplet.

Experimental Section

General Methods. NMR spectra were recorded on a JEOL 200-MHz Fourier transform spectrometer with tetramethylsilane as an internal standard. Ultraviolet and visible absorption spectra were measured with a Hewlett-Packard 8450A spectrometer. Elemental analyses were performed by Galbraith Laboratories of Knoxville, TN. Triplet-sensitized reactions were conducted on nitrogen-purged samples placed in a 250-mL photochemical reaction vessel with a 450-W Hanovia medium-pressure mercury lamp enclosed in a water-cooled Pyrex immersion well. A uranium glass filter was used to eliminate wavelengths below 340 nm. Alternatively, a Pyrex filter was used to eliminate wavelengths below 300 nm. Analytical irradiations and quantum yield measurements were conducted under dry N_2 in a 100-mL Pyrex rectangular reactor. Irradiated mixtures were analyzed on a Hewlett-Packard 5710A gas chromatograph equipped with flame ionization detectors. Preparative gas chromatography was performed on F & M Lab Chromatograph Model 700.

Materials: General. The following reactants were used as received from Aldrich: cyclopropyl bromide, cyclopropyl phenyl ketone, cyclopropanecarboxaldehyde, cyclopentanone, magnesium metal, dicyclopentadiene, methyltriphenylphosphonium bromide, benzyltriphenylphos-

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† Adapted from the M.S. Thesis of Lingwen Zhou, The University of Texas at Dallas, December, 1990.

® Abstract published in *Advance ACS Abstracts,* February 1, 1994.

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phonium bromide, 2.5 M butyllithium/hexane solution, 3.0 M phenylmagnesium bromide solution in diethyl ether, and 1.0 M potassium *tert*-butoxide solution in tetrahydrofuran. Both 1-indanone and 2-indanone (Aldrich) were chromatographed on silica gel and recrystallized twice from hexane. DMF was refluxed over calcium hydride and distilled. Ether was distilled from LiAlH$_4$ prior to use. Cyclopentadiene was distilled from dicyclopentadiene dried over LiAlH$_4$ and used immediately. Benzene (Aldrich) was distilled prior to use. All sensitizers were recrystallized from proper solvents to constant melting points.

α-Cyclopropylstyrene (2)[13] **and β-Cyclopropylstyrenes (1)**[14] were prepared by Wittig reactions according to literature procedures, the former from methyltriphenylphosphonium bromide and cyclopropyl phenyl ketone (0.07 mol) and the latter from benzyltriphenylphosphonium bromide and cyclopropanecarboxaldehyde (0.06 mol). The former (5.2 g) was obtained in 48% yield. The isomers of β-cyclopropylstyrene were separated by spinning band distillation, yielding *cis*-β-cyclopropylstyrene, 2.4 g, bp 58–60 °C (0.40 mm), and *trans*-β-cyclopropylstyrene, 5.1 g, bp 63-65 °C (0.43 mm), 75% overall. Each compound had a ^{1}H NMR spectrum consistent with the assignment and was homogeneous to gas chromatography.

1-Phenylcyclopentene[15] **and 3-Phenylcyclopentene (5)**[15,16] were prepared according to literature procedures.

α-Cyclopropyl-(3*H*)-indene (3). To a solution of cyclopropylmagnesium bromide, prepared from 3.88 g of cyclopropyl bromide (32 mmol) and 0.93 g of magnesium turnings (32 mmol) in 26 mL of dry ether under nitrogen atmosphere, was added dropwise a solution of 4.23 g of 1-indanone (32 mmol) in 10 mL of dry ether. The mixture was allowed to stir overnight at 25 °C. The reaction was quenched with 50 g of crushed ice, acidified with 50 mL of 20% aqueous sulfuric acid, and refluxed for 3 h. After dilution with water, ether extraction, and washing of the extracts with water, saturated sodium bicarbonate, and brine, followed by drying over anhydrous sodium sulfate, the solvent was evaporated. The oily residue was chromatographed on 120 g of 70–230 mesh silica gel using 50:50 benzene:hexane as eluent. Distillation gave 1.8 g of slightly colored product. Further purification via Kugelrohr distillation yielded 1.5 g of α-cyclopropyl-(3*H*)-indene (30% yield): ^{1}H NMR (CDCl$_3$, TMS) δ 7.54–7.16 (m, 4H), 6.01 (s, 1H), 3.20 (s, 2H), 1.85–1.26 (m, 1H), 0.88 (m, 2H) 0.66 (m, 2H); ^{13}C proton-decoupled NMR (CDCl$_3$, TMS) δ 146.8, 145.5, 144.2, 126.1, 124.7, 124.5, 118.5, 37.1, 8.2, 6.2. Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 91.11; H, 7.63.[17]

β-Cyclopropyl-(3*H*)-indene (4). 2-Indanone (4.20 g, 32 mmol) in 10 mL of dry ether was added slowly to a solution of cyclopropylmagnesium bromide (from 3.92 g of cyclopropyl bromide and 0.95 g of Mg metal) in 25 mL of dry ether under nitrogen atmosphere. The solution was stirred overnight and hydrolyzed with 40 mL of saturated aqueous ammonium chloride. The reaction mixture was diluted with 100 mL of water, and the product was extracted with ether. After workup, the crude product consisted of a dark brown viscous oil which was added directly to 70 mL of 20% aqueous sulfuric acid. The solution was refluxed for 3 h, cooled to room temperature, and taken up in ether. The ethereal extracts were washed with water, 10% NaHCO$_3$, water, and brine. After the mixture was dried (MgSO$_4$), the ether was removed by rotary evaporation and the residue was chromatographed on 60 g of 70–230 mesh silica gel (CH$_2$Cl$_2$ eluent). The first component to come off the column was collected and distilled, yielding 1.1 g of β-cyclopropyl-(3*H*)-indene (22% yield); ^{1}H NMR (CDCl$_3$, TMS) δ 7.31–7.10 (m, 4H), 6.50 (s, 1H), 3.18 (s, 2H), 1.82–1.51 (m, 1H), 0.90 (m, 2H), 0.66 (m, 2H). Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 91.91; H, 7.44.

Irradiations. α-Cyclopropylstyrene (2). A nitrogen-purged solution of 1.01 g (7 mmol) of **2** in 230 mL of dry benzene containing 3.01 g of benzophenone was irradiated in a 250-mL photochemical reaction vessel with a Pyrex-filtered 450-W Hanovia medium-pressure mercury lamp enclosed in a water-cooled Pyrex immersion well. Monitoring the photolysis by GLC after 24 h showed no significant disappearance of **2** and no detectable appearance of photoproduct. The solvent was then removed by a rotary evaporator, and the residue was chromatographed over silica gel (120 g, 70–230 mesh) using benzene as the eluting solvent. The first fraction was a colorless oil (0.78 g) whose ^{1}H NMR spectrum was identical with that of authentic **2**: ^{1}H NMR (CDCl$_3$, TMS) δ 7.61–7.29 (m, 5H), 5.27 (s, 1H), 4.93 (s, 1H), 1.65 (m, 1H), 0.85–0.55 (m, 4H). The second fraction contained Ph$_2$CO as white crystals (2.05) g), mp 48–50 °C.

cis*-β-Cyclopropylstyrene (*cis*-1).** A nitrogen-purged solution of ***cis*-1** (1.03 g, 7.1 mmol) in benzene (250 mL) containing 3.03 g of benzophenone was irradiated similarly. Monitoring the photolysis by GLC showed a gradual disappearance of ***cis*-1** and the concomitant appearance of two photoproducts (trans*-1,5**) identified by their GLC retention times. The *trans*/*cis* ratio was constant at 64:36 after 0.5 h of irradiation. Slow growth of **5** was then observed from prolonged irradiation. The concentration of **5** became stationary after 24 h at about 20% of the initial **1**. The oil remaining after removal of solvent was chromatographed on a silica gel column (120 g, 70–230 mesh) with hexane:ethyl acetate (98:2) as eluent to remove benzophenone. The resulting oil was further separated *via* preparative GLC, isolating 3-phenylcyclopentene of 98% GLC purity, ***trans*-1** (GLC pure), and ***cis*-1** (GLC pure), with spectral properties indistinguishable from those of authentic material.

***trans*-β-Cyclopropylstyrene (*trans*-1).** A nitrogen-purified solution of ***trans*-1** (1.09 g, 7.5 mmol) in benzene (230 mL) containing 3.01 g of benzophenone was subjected to the same irradiation conditions with results identical to those for the *cis* isomer. The oil remaining after removal of solvent was chromatographed on a silica gel column (120 g, 70–230 mesh) with hexane:ethyl acetate (98:2) as eluent to remove benzophenone. The resulting oil was further separated *via* preparative GLC, affording 3-phenylcyclopentene of 99% GLC purity, 98% GLC pure ***cis*-1**, and 96% GLC pure ***trans*–1**.

α-Cyclopropyl-(3*H*)-indene (3). A nitrogen-purged solution of **3** (234 mg, 1.5 mmol) in benzene (30 mL) containing 40 mg of xanthone was irradiated through a uranium glass filter (Corning 3320) in a Pyrex rectangular reactor in proximity to the lamp well. Monitoring the photolysis by GLC after 48 h showed 23% disappearance of **3** and no detectable appearance of photoproduct. After removal of the solvent, the residue was chromatographed on silica gel using benzene as eluent to remove xanthone. The resulting oil was purified *via* Kugelrohr distillation, yielding 176 mg (75%) of **3**, pure to GLC and NMR.

β-Cyclopropyl-(3*H*)-indene (4). A nitrogen-purged solution of **4** (246 mg, 1.6 mmol) in benzene (30 mL) containing 42 mg of xanthone was irradiated through a uranium glass filter in a Pyrex rectangular reactor. Monitoring the photolysis by GLC after 48 h showed 5% disappearance of **4** and no detectable appearance of photoproduct. After removal of the solvent, the residue was chromatographed on silica gel using benzene as eluent to remove xanthone. The resulting oil was purified *via* Kugelrohr distillation, yielding 230 mg (93%) of **4**, pure to GLC and NMR.

Laser Flash Photolysis. Transient spectroscopic experiments were conducted according to procedures described previously at the Center for Fast Kinetics Research (CFKR)[18] at The University of Texas at Austin and in our laboratory.[1,19] All experiments were in nitrogen- or argon-sparged benzene with thioxanthone (E_T 65.5 kcal/mol)[20] sensitization to take advantage of the absorption window from 295–335 nm. Excitation was at the third harmonic (355 nm) of a mode-locked Nd:YAG laser, with pulse extended to 200 ps FWHM, in all cases.

Quantum Yields. Quantum yields for formation of **5** from the β-cyclopropylstyrenes were measured relative to *trans*-β-methylstyrene isomerization, taking Φ_{t-c} for *trans*-β-methylstyrene as 0.5.[21] Photolyses were conducted with 0.4 mM thioxanthone and 0.033–0.037 mM arylalkene in 30 mL in a 100-mL Pyrex rectangular reactor using a Hanovia medium-pressure 450-W mercury arc UV lamp. The reactor was held at constant distance from the light source. The optical density of the solutions was the same (within 10%) for each sensitized irradiation. Each solution contained chlorobenzene as internal standard. All solutions were sparged with nitrogen before and during photolysis. The lamp was allowed to warm up for 30 min before samples were put in place. The photolyses were analyzed by GLC (10% OV-17, 10 ft, 170 °C) at various intervals, every 3–4 min for *trans*-β-methylstyrene and hourly for the cyclopropylstyrenes. The product vs time dependence was constant within about 10% for replicate experiments.

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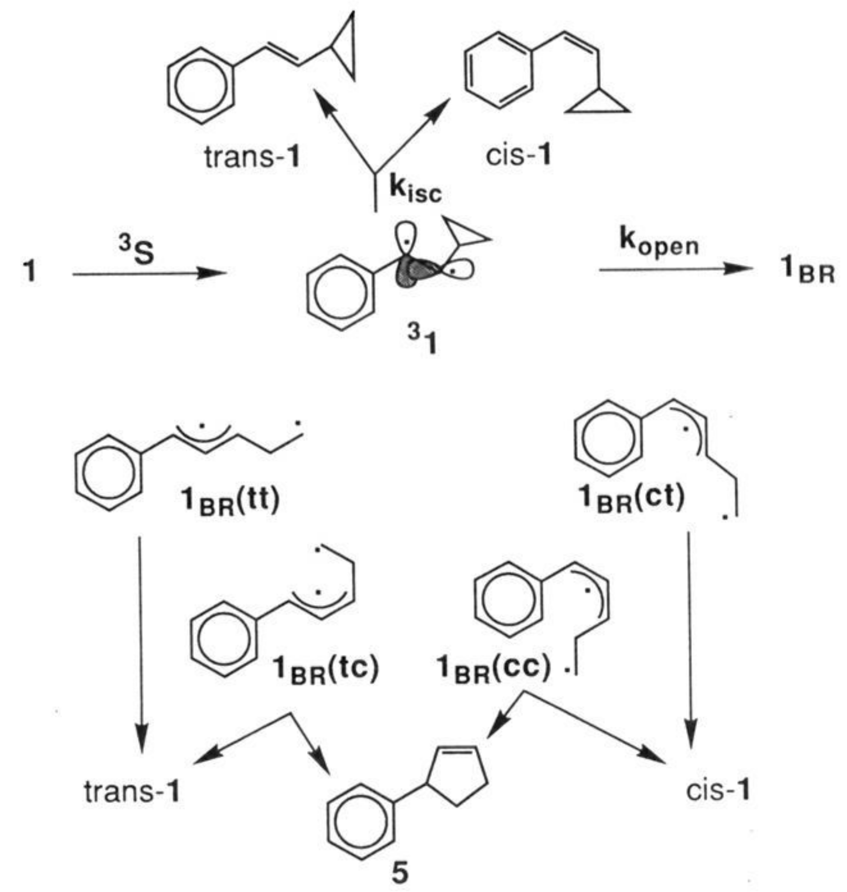
Scheme 1



Results

Photolysis in benzene ($\lambda > 340$ nm) of either ***cis*-1** or ***trans*-1** (β-cyclopropylstyrene) with thioxanthone as triplet sensitizer led slowly ($\phi \approx 2 \times 10^{-3}$) to 3-phenylcyclopentene **5** following rapid establishment ofa photostationary mixture of ***cis*-1** (36%) and ***trans*-1** (64%). The photostationary state contrasts with the *cis*-rich value (70% *cis*:30% *trans*) for β-methylstyrene with thioxanthone sensitization.[21] There is no precedent for the change in a simple alkyl group causing such a substantial change in the photostationary state when the mechanism for establishing the photostationary state is the ordinary triplet excitation transfer and subsequent alkene triplet decay to the ground-state geometric isomers *via* intersystem crossing (ISC).

However, both the unexpected photostationary state and the formation of **5** can be accounted for by Scheme 1. The essence of Scheme 1 is the cyclopropylcarbinyl opening of $^{3}\mathbf{1}$ to $\mathbf{1}_{\mathbf{BR}}$, which must contribute substantially, i.e., at least comparably to the ordinary $T_1 \rightarrow S_0$ ISC mechanism. There are four possible geometric isomers of $\mathbf{1}_{\mathbf{BR}}$. Of these, the α,β-*trans* biradicals $\mathbf{1}_{\mathbf{BR}}$**(tt)** and $\mathbf{1}_{\mathbf{BR}}$**(tc)** are the more stable since steric inhibition of conjugation of the phenyl and allyl moieties raises the energies of the α,β-cis structures $\mathbf{1}_{\mathbf{BR}}$**(ct)** and $\mathbf{1}_{\mathbf{BR}}$**(cc)**. The trans-rich photostationary state may be rationalized *post hoc* by a steric preference for ring opening to afford the all-*trans* (and thus most stable) $\mathbf{1}_{\mathbf{BR}}$**(tt)**, since it can form only *trans*-**1** following T–S ISC and cyclopropyl ring closure. Closure to form the 5-membered ring gives **5**. Only the biradicals $\mathbf{1}_{\mathbf{BR}}$**(tc)** and $\mathbf{1}_{\mathbf{BR}}$**(cc)** can form **5**, because $\mathbf{1}_{\mathbf{BR}}$**(tt)** and $\mathbf{1}_{\mathbf{BR}}$**(ct)** would lead to an impossibly strained *trans*-cyclopentene. The low quantum yield of formation of **5** indicates that reclosure of the cyclopropane is predominant.

In contrast, **2** and **4** were, in our hands, chemically inert to sensitized photolysis. Slow disappearance of **3** might be due to dimerization analogous to indene.[22]

Transient Spectroscopy. Assignments and Lifetimes of Transients. For all cases, the only transients expected are the triplets ^{3}**(1-4)** and the cyclopropyl ring-opened biradicals **(1-4)**$_{\mathbf{BR}}$. The issue in each case is the determination of which of these the observed transient(s) is (are).

Transient spectroscopy of **1** and **2** (0.14 M) in benzene revealed identical nanosecond transients in each case. At this concentration, the time scale of triplet excitation transfer from sensitizer is *ca.* 1.4 ns, calculated from our measured values of excitation transfer from thioxanthone is ***cis*-1** (4.6×10^{9} M^{-1} s^{-1}) and ***trans*-1** (5.2×10^{9} M^{-1} s^{-1}). In either case, this is much faster than, and thus not a perturbation on, the lifetimes of the transients here reported. Either ***cis*-1** or ***trans*-1** affords a biphasic rise and decay (Figure 2) with $\lambda_{max} \approx 315$ nm and lifetimes of 7 and 17 ns, respectively. Either transient is faster than the decay of β-methylstyrene triplet ($\tau = 27$ ns[4]) but is consistent either with $^{3}\mathbf{1}$ accelerated by the ring opening or with the acyclic 1,3-biradical ($\tau \approx 7$–18 ns[23,24]) $\mathbf{1}_{\mathbf{BR}}$. We assign the two lifetimes accordingly to $^{3}\mathbf{1}$ and $\mathbf{1}_{\mathbf{BR}}$ but cannot tell which is which. Note that in sequential first-order kinetics the fastest process is always observed as the first process, even though its rate may correspond to the second step.[25]

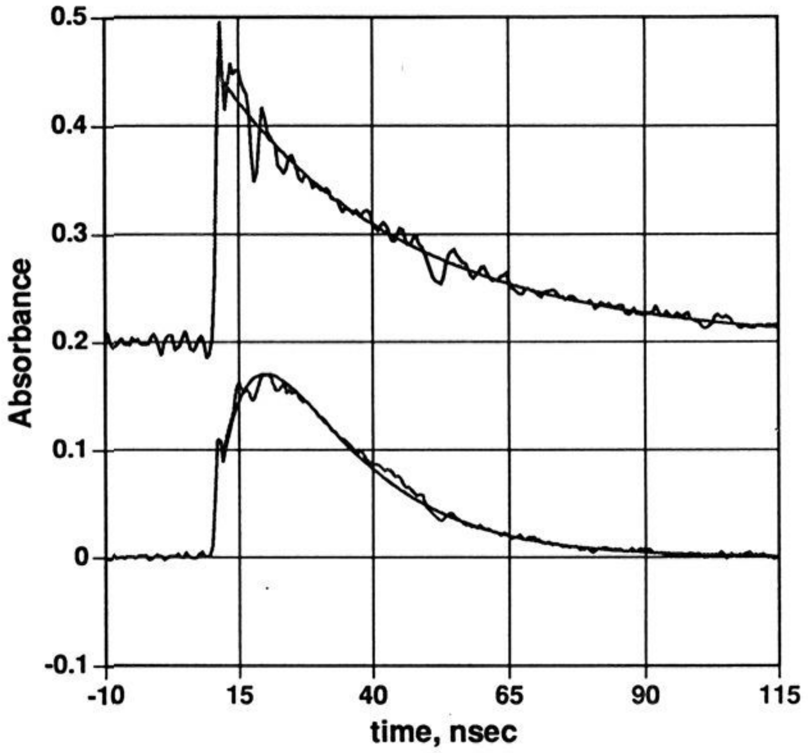


Figure 2. Transients from α-cyclopropylstyrene (**2**) (top, shifted by 0.2 absorbance units) and β-cyclopropylstyrene (**1**) (bottom) observed at 310 nm, with fits corresponding to the parameters in the text.

From **2**, only a prompt transient ($\lambda_{max} \approx 315$ nm, $\tau = 35$ ns) results. It is assigned as $^{3}\mathbf{2}$ by analogy to the *p*-methoxy-α-methylstyrene triplet ($\tau = 31$ ns[12]) and by the apparent absence of a biradical $\mathbf{2}_{\mathbf{BR}}$ as judged from the chemical inertness.

The transient from **3**, $\lambda_{max} \approx 360$ nm, exhibits a modest dependence on the concentration of **3**: k_{decay} (s^{-1}) = $(4.25 \times 10^{6}) + (2.7 \times 10^{7})$[**3**]; $\tau = 235$ ns after extrapolation to [**3**] = 0. The second-order rate constant is near that for quenching of indene triplets by ground state indene (5×10^{7} M^{-1} sec^{-1}), and the λ_{max} is only slightly shifted from the 350 nm we observe for indene triplet, leading to assignment of the transient as $^{3}\mathbf{3}$ and not $\mathbf{3}_{\mathbf{BR}}$. Since the spectroscopic triplet energy of the indene chromophore is 65 kcal/mol[4] and that of isoprene is 60 kcal/mol, we also used isoprene quenching as a test for assignment as an indene-like triplet. The transient from **3** was indeed quenched by isoprene ($k_q = 1.05 \times 10^{9}$ M^{-1} s^{-1}), whereas triplet 1,3-biradicals are not.[23] Its assignment as $^{3}\mathbf{3}$ thus seems secure.

The transient from **4** ($\tau = 15$ ns) showed λ_{max} *ca.* 330 nm. Since the lifetime is so short, absence of dependence on [**4**] ground-state concentration is not informative. This transient is not quenched by isoprene ($k_q < 2.5 \times 10^{7}$ M^{-1} s^{-1}) and is thus not an indene-type triplet $^{3}\mathbf{4}$. The lifetime and the absence of quenching by isoprene are consistent with the behavior of triplet 1,3-biradicals with freely rotating termini, *cf.* those from diarylcyclopropanes.[23] The appropriateness of the comparison of lifetime for a cinnamyl-unconjugated alkyl biradical with that

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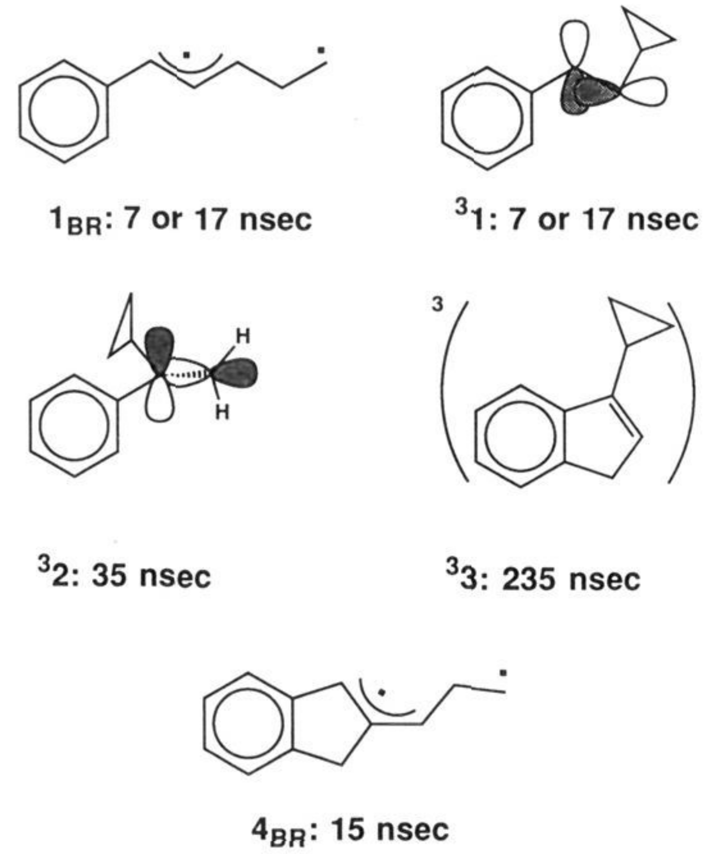
Chart 1



for a bis-benzylic biradical might be questioned. However, the extent of conjugation at a biradical terminus has a rather modest effect on the lifetime, with increased conjugation causing a modest lifetime increase[26] when the lifetime is controlled by ISC. In this case, the model has less conjugation on one side but more on the other, which we expect to produce opposing modest effects and therefore a quite small net effect. On this basis, we assign the transient from **4** as the ring-opened biradical $\mathbf{4}_{\mathbf{BR}}$.

Chart 1 depicts the transients assigned with their lifetimes.

Discussion

Rates of Ring Opening of Triplets. The central issue in this work is the comparison of the rates of cyclopropyl ring opening from the triplet states of the reactants with the rates of ring opening of appropriate cyclopropylcarbinyl radical models. In general, the (inverse) lifetimes of the triplets are determined by the two competing processes, k_{open} and k_{ISC}, with $(\tau_{\mathrm{obs}})^{-1} = (k_{\mathrm{open}} + k_{\mathrm{ISC}})$ and with the probability of opening given by $k_{\mathrm{open}}/(k_{\mathrm{open}} + k_{\mathrm{ISC}})$. We use this analysis repeatedly below to obtain k_{open} from $(\tau_{\mathrm{obs}})^{-1}$ and reasonable models for k_{ISC}.

For ^{3}**3**, k_{open} is obtained straightforwardly. The lifetime of ^{3}**3** is substantially shorter than that of the indene triplet (1.4 μs[27]); we assign the rate increase to ring opening. Assuming that the rate of spontaneous decay is the same as that for indene, the rate constant for ring opening of ^{3}**3** is $(235\ \mathrm{ns})^{-1} - (1.4\ \mu\mathrm{s})^{-1} = 3.5 \times 10^{6}\ \mathrm{s}^{-1}$.

For ^{3}**4**, k_{open} is only available as a lower limit. It must be faster than the rise rate for the transient biradical observed, since ^{3}**4** is its precursor. The biradical risetime is prompt within the detector resolution. Moreover, the intensity of the biradical is essentially constant as a function of isoprene concentration. Therefore, there is no significant quenching of ^{3}**4** by isoprene, yet the results for **3** would suggest a rate constant near $10^{9}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. We estimate $5 \times 10^{8}\ \mathrm{s}^{-1}$ as a lower limit for ring opening of ^{3}**4**.

For ^{3}**2**, k_{open} is, in contrast, only available as an upper limit, since its lifetime is normal. We assume that the 1,5-closure would have the same probability from the triplet as for ^{3}**1**. Less than 0.5% of the relevant product 1-phenylcyclopentene was formed under conditions in which ^{3}**1** afforded 20% of 3-phenylcyclopentene, giving a probability of opening <1/40 that for ^{3}**1**. We take the 7-ns lifetime from **1** as that of ^{3}**1** for present argument since the calculation of opening probability (*vide infra*) gives the higher probability (*ca.* 75%) of opening. We thus obtain a probability of opening for ^{3}**2** of <0.02. Accordingly, the rate of ring opening for ^{3}**2** is $<0.02(35\ \mathrm{ns})^{-1} = 6 \times 10^{5}\ \mathrm{s}^{-1}$.

Table 1. Rates of Ring Opening of Triplets

triplet	rate constant k_{open}, s^{-1}
β-cyclopropylstyrene (**1**)	$1.6 \times 10^{7} < k_{\mathrm{open}} < 1.1 \times 10^{8}$
α-cyclopropylstyrene (**2**)	$<6 \times 10^{5}$
α-cyclopropyl-(3*H*)-indene (**3**)	3.5×10^{6}
β-cyclopropyl-(3*H*)-indene (**4**)	$>5 \times 10^{8}$

Ring opening of ^{3}**1** is subject to the ambiguity mentioned above. It is not possible to assign either the 7- or the 17-ns lifetime to the triplet with certainty. It is easy to assign an upper limit to the rate of opening of ^{3}**1** from the assumption that it derives from the faster process observed. Since then $(\tau_{\mathrm{obs}})^{-1} = 1.43 \times 10^{8}$, and since k_{ISC} should be about $3.7 \times 10^{7}\ \mathrm{s}^{-1}$ from the known[4] lifetime of β-methylstyrene triplet (27 ns) as a model, the upper limit for the ring-opening rate is accordingly $1.1 \times 10^{8}\ \mathrm{s}^{-1}$.

The lower limit for the rate of ring opening of ^{3}**1** is more problematic. The unknown rate of ISC of ^{3}**1** contributes more percentagewise than to the upper limit. Most simply, the application of the reasoning above to the 17-ns lifetime affords $2.2 \times 10^{7}\ \mathrm{s}^{-1}$ for the rate of opening. A second way of estimation is to assume that the 36:64 photostationary ratio of ***cis*-1** to ***trans*-1** derives from a mixture of two decays, one through the usual ISC for ^{3}**1** and one derived from biradical formation *via* ring opening and 1,3-ring closure in the biradical. Considering the small difference in excitation rate constants for ***cis*-1** and ***trans*-1** (*vide infra*), the photostationary ratio allows a net decay ratio from ^{3}**1** of ***cis*-1**:***trans*-1** = 33:67. Obviously the biradical formation pathway must lead to *trans*-rich product since there is no reason to expect much if any difference from the usual 50:50 *cis*:*trans* decay ratio, known[21,28] for other β-alkylstyrenes, *via* ISC of ^{3}**1**. The assumption that all ***cis*-1** in the decay derives from the ISC path then allows calculation as follows of a lower limit of the fraction of decay of ^{3}**1** *via* the biradical pathway. The amount of ***trans*-1** *via* ISC should equal that of ***cis*-1** if their ratio *via* ISC is 50:50, and thus from the 33:67 decay ratio, 34% of total decay remains to be assigned to decay *via* the ring opening. The rate of opening is thus at least $0.34(17\ \mathrm{ns})^{-1} = 2 \times 10^{7}\ \mathrm{s}^{-1}$ and will be greater if, as seems reasonable, not all ***cis*-1** in the decay derives from the ISC path. Allowing the ratio *via* ISC to increase somewhat to 1.2:1 favoring *trans* leads to a minimum rate of opening of $1.6 \times 10^{7}\ \mathrm{s}^{-1}$. There is no reason to expect any deviation from 50:50 at all, but the 1.2:1 assumption is offered somewhat arbitrarily to exemplify the effect of the decay ratio. The agreement between these estimates gives confidence that we know the lower limit but is accidental.

Table 1 summarizes the rates of ring opening of ^{3}**1**–^{3}**4**. The variation of at least 3 orders of magnitude in the rates is remarkable considering that all reactants have the cyclopropyl group pendant on the same chromophore.

Structural Dependence of the Rates of Ring Opening. Table 1 shows clearly that the cyclopropyl groups in the β position undergo opening at least some 2 orders of magnitude more rapidly than their α counterparts. Also, the rate of opening at each (α or β) position is enhanced in the planar indene triplets relative to the other two perpendicular triplets. Each of these is readily explicable by the 1,2-biradical model.

Newcomb *et al.*[29] have observed rate constants in the range of $(4\text{–}5) \times 10^{11}\ \mathrm{s}^{-1}$ for 2-phenyl- and 2,2-diphenylcyclopropylcarbinyl opening at 25 °C, accelerated by several thousandfold from

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cyclopropylcarbinyl itself, providing precedent for acceleration of ring opening by increased exothermicity. That the indene derivatives should have enhanced reactivity then follows from their relatively high triplet energy. Relaxed perpendicular styrenes have E_T = 51–54 kcal/mol, while indene has a relaxed E_T = 65 kcal/mol.[4] The extra energy for the latter translates into some 11–14 kcal/mol greater exothermicity for biradical formation, since the extents of delocalization in $\mathbf{3}_{\mathbf{BR}}$ *vs* $\mathbf{2}_{\mathbf{BR}}$ and in $\mathbf{4}_{\mathbf{BR}}$ *vs* $\mathbf{1}_{\mathbf{BR}}$ do not differ. That the ring opening is much faster for β-cyclopropyl derivatives than for α-cyclopropyl derivatives follows from consideration of the triplets as 1,2-biradicals: in the β case, the terminus bearing the cyclopropyl group is analogous to an α-alkylcyclopropylcarbinyl radical, while in the α case, the terminus is analogous to an α-arylcyclopropylcarbinyl radical. The cyclopropylcarbinyl radical itself undergoes ring opening exothermically, by about 4 kcal/mol,[7,30] and α-alkylcyclopropylcarbinyl radicals should not differ significantly. The α-arylcyclopropylcarbinyl radical enjoys resonance stabilization from the phenyl, estimated from bond dissociation energies for toluene[31] and ethane[32] at about 13 kcal/mol. Accordingly, the cyclopropylcarbinyl opening in the latter case should be about 9 kcal/mol endothermic and consequently far slower. Contributing additionally in the comparison of **1** to **2** (and also **4** to **3**) is the slightly more stable cinnamyl moiety in $\mathbf{1}_{\mathbf{BR}}$ and $\mathbf{4}_{\mathbf{BR}}$ *vs* the 2-phenylallyl moiety in $\mathbf{2}_{\mathbf{BR}}$ and $\mathbf{3}_{\mathbf{BR}}$. Opening of $^3\mathbf{1}$ is discussed further below. That opening of $^3\mathbf{2}$ is in fact unobserved is therefore reasonable. The openings of $^3\mathbf{3}$ and $^3\mathbf{4}$ are, by the same rough estimation, exothermic by 2–5 and 15–19 kcal/mol, respectively. *The observed order of reactivity in Table 1 is thus in good agreement with the estimated exothermicity.*

Comparison with Known Rates for Cyclopropylcarbinyl Opening. If the 1,2-biradical model is to have full quantitative validity, absolute rates of reaction should also be predictable. We chose to study cyclopropylcarbinyl opening because absolute rates for appropriate free-radical models were available, at least for $^3\mathbf{1}$ and $^3\mathbf{2}$. The appropriate comparison for $^3\mathbf{1}$ is an α-alkylcyclopropylcarbinyl radical. Several examples are known, *cf.* α-methylcyclopropylcarbinyl. There are at least two reliable kinetic studies of this radical. The values which we calculate for α-methylcyclopropylcarbinyl at 25 °C from the activation parameters reported by Burkhard *et al.* (1.3×10^7 s^{-1})[33] and by Bowry *et al.* (5.3×10^7 s^{-1})[34] (which activation parameters differ somewhat from each other) are in remarkably good agreement with the rate constant range for opening of β-cyclopropylstyrene triplet in Table 1. The latter authors also report rate constants for opening of 1-(2-ethylcyclopropyl)ethyl radicals (8.6×10^7 s^{-1}) and 1-(1-ethylcyclopropyl)ethyl radicals (3.2×10^7 s^{-1}) calculated similarly for 25 °C. We could not have asked for better agreement if we had made these numbers up! The results of Bowry *et al.* suggest that the range of variation in rate constant with differing alkyl substitution on the cyclopropylcarbinyl moiety is small, possibly adding credence to our approximation of the benzyl radical group as a methyl.

Masnovi *et al.* report a rate constant range of $(0.5–3.9) \times 10^5$ s^{-1} for ring opening of a series of α-phenylcyclopropylcarbinyl radicals at room-temperature.[35] This range includes both secondary and tertiary radicals as well as examples with substituents in the phenyl ring. Our value for $^3\mathbf{2}$ is an upper limit, and it is somewhat higher than these values, as it should be. The expected large effect of the α-phenyl in retarding opening is clear both for alkene triplets and for cyclopropylcarbinyl radicals.

Chemistry of Closure. The formation of 3-phenylcyclopentene *via* $\mathbf{1}_{\mathbf{BR}}$ occurs with a quantum yield *ca.* 2×10^{-3}. Since, based on the kinetics we observe, opening of $^3\mathbf{1}$ must have a much higher probability than that, there must be a source of inefficiency. A 1,3-closure to regenerate either ***trans*-1** or ***cis*-1** is almost certainly the source of the inefficiency. This is reasonable, since (1) 1,3-closure is favored by proximity (i.e., probability) and (2) some geometric isomers of $\mathbf{1}_{\mathbf{BR}}$ which may form are incapable of affording 3-phenylcyclopentene except in a trans form, which surely is too high in energy to be attained. The photochemical inertness of **3** and **4** probably also reflects a very strong preference for 1,3- rather than 1,5-closure for similar reasons.

Conclusion

We conclude that the answer to the title question is yes, as far as the cyclopropylcarbinyl clock is concerned. Absolute rate constants and the effect of constraint to planarity are both satisfactorily understood. We are studying the general question further using additions and abstractions as clock reactions.

Acknowledgment. This work was supported by National Science Foundation Grants CHE-8820268 and 9121313. Preliminary flash photolysis experiments were performed at the Center for Fast Kinetics Research at The University of Texas at Austin, supported by NIH Grant RR-00886 from the Biotechnology Branch of the Division of Research Resources and by The University of Texas at Austin.

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