# Cyclopropylcarbinyl Ring Opening as Mechanistic Probe for Differentiation between the Singlet and Triplet Spin States of Trimethylenemethane Diradicals (Non-Kekulé Species)

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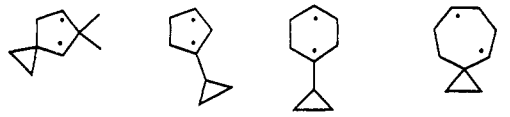
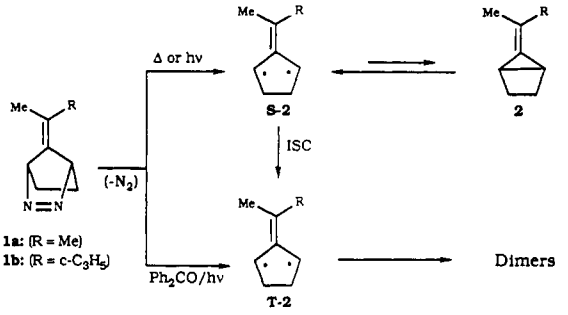
**Abstract:** The cyclopropylcarbinyl rearrangement of the non-Kekulé 2-alkylidene-1,3-cyclopentanediyl diradical (S-**2b** and T-**2b**), generated by thermal and direct and triplet-sensitized photochemical denitrogenation of the corresponding azoalkane **1b**, was explored. While in the triplet-sensitized photolysis at moderate temperatures no cyclopropylcarbinyl rearrangement took place, in the singlet manifold (thermolysis and direct photolysis) the rearranged hydrocarbon **3** was observed. The amount of the rearranged hydrocarbon **3** increased with increasing temperature, and from the temperature dependence, an activation energy of ca. 5 kcal/mol was estimated for the ring opening. The intact triplet 1,3-diradical T-**2b** and its ring-opened triplet 1,6-diradical T-**2b'** were trapped by $^3O_2$ in the form of their stable endoperoxides **5** and **6**. Under the trapping conditions, dimerization of the triplet species T-**2b** was completely eliminated through dioxygen trapping. Also, 1,4-cyclohexadiene served as a scavenger for the T-**2b** diradical through hydrogen atom transfer, but less effectively since much dimer was still observed. The present study constitutes the first example of the cyclopropylcarbinyl rearrangement of a non-Kekulé species, in particular the singlet diradical S-**2b**. Of mechanistic significance is the observation that the much longer lived triplet diradical T-**2b** does not undergo ring opening. The reason for this is the special trimethylenemethane stability of the ground-state triplet diradical T-**2b**, which imposes a higher activation energy for ring opening ($E_a$ ca. 14 kcal/mol) than usual ($E_a$ ca. 5 kcal/mol), and consequently cyclopropylcarbinyl rearrangement cannot compete with dimerization ($E_a$ < 2 kcal/mol).

In recent years, cyclopropylcarbinyl rearrangements have been subject to intensive experimental and theoretical investigations, especially as a mechanistic probe for radical reactions.[1] The activation barrier for ring opening is about 6 kcal/mol,[1c] which lies in an ideal range for serving as an effective cyclopropylcarbinyl clock to estimate lifetimes of diradical intermediates. The known




examples of lifetimes of localized diradical species studied by the cyclopropylcarbinyl clock are shown here, which include trimethylene and tetramethylene derivatives.[2] These four cases concern triplet lifetimes, because triplet diradicals can be long-lived enough[3] to experience the cyclopropylcarbinyl rearrangement. However, to date no examples of such rearrangements appear to be documented for singlet diradicals, presumably the consequence of their much shorter lifetimes.

It was our interest to apply the cyclopropylcarbinyl ring opening as a mechanistic probe to non-Kekulé species, namely, the cross-conjugated trimethylenemethane diradicals, of which particularly the 2-isopropylidene-1,3-cyclopentanediyl derivative **1a** has been extensively investigated (eq 1).[4] Accessible through




(1)

thermal or photochemical denitrogenation of the corresponding azoalkane **1a**, in its singlet state, the diradical S-**2a** cyclizes into the highly strained housane **2a** or undergoes intersystem crossing (ISC) to its triplet state T-**2a**; the latter dimerizes. Housane **2a** persists only at about −60 °C; on warming it ring opens back to S-**2a** which, after ISC to T-**2a**, dimerizes. The ISC process S-**2a** → T-**2a** is very efficient in view of the fact that T-**2a** is lower in energy than S-**2a** by ca. 15 kcal/mol and is thus the ground state of the diradical (Figure 1).

A particular advantage for our purpose of probing for cyclopropylcarbinyl rearrangements in non-Kekulé species are the relatively long lifetimes of the diradical **2a**, namely, 0.28 ns[4b] for the singlet and 916 ns[5] for the triplet state. By replacing the methyl with a cyclopropyl group, even the singlet species S-**2b** should undergo cyclopropylcarbinyl ring opening to a sufficient extent to observe rearranged products. In fact, in view of the large energy gap ($\Delta E_{ST}$ is ca. 15 kcal/mol) between the singlet and triplet states of the trimethylenemethane-type non-Kekulé diradicals **2** in favor of the triplet state, the latter possesses a special stability[6] and ISC back to S-**2** is highly improbable; thus, dimerization ($E_a$ < 2 kcal/mol) prevails. Moreover, for the par-

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**Table I.** Product Distribution of the Thermolyses and Photolyses of the Azoalkane **1b**

| entry | reaction conditions | | mass-balance (%)[a] | product distribution (%)[b,c] 3 | dimer ($C_{20}H_{28}$) | trapping products[d] |
|---|---|---|---|---|---|---|
| | | Thermolyses | | | | |
| 1 | 80 °C, $C_6H_6$, 1 h | Ar | >95 | 59 | 41 | 0 |
| 2 | 160 °C/0.01 Torr | | >93 | 91 | 9 | 0 |
| 3 | 60 °C, $C_6H_{12}$, 2 h | $O_2$ | 80 | 25 | 0 | 68 (**5**)<br>7 (**6**) |
| 4 | 80 °C, $C_6H_6$, 5 h | 1,4-cyclohexadiene | >90 | 32 | 8 | 12 (**4**)<br>8 ($C_{20}H_{30}$)<br>20 ($C_{16}H_{22}$) |
| | | Direct Photolyses[e] | | | | |
| 5 | 350 nm, $CFCl_3$, −78 °C, 4 h | Ar | 89 | 2 | 91 | 0 |
| 6 | 350 nm, $CFCl_3$, 0 °C, 4 h | Ar | 93 | 9 | 86 | 0 |
| 7 | 350 nm, $C_6H_6$, 10 °C, 4 h | Ar | 87 | 13 | 82 | 0 |
| 8 | 350 nm, $C_6H_6$, 25 °C, 4 h | Ar | 84 | 25 | 64 | 0 |
| 9 | 350 nm, $C_6H_{12}$, 20 °C, 15 min | $O_2$ | 85 | 15 | 0 | 85 (**5**) |
| 10 | 333 nm, $C_6H_6$, 6 °C, 4 h | 1,4-cyclohexadiene | >90 | 10 | 80 | 1 (**4**) |
| | | Benzophenone-Sensitized Photolyses[f] | | | | |
| 11 | 364 nm/$Ph_2CO$, $C_6H_6$, 6 °C | Ar | 85 | 2 | 85 | 0 |
| 12 | 364 nm/$Ph_2CO$, $C_6H_{12}$, 20 °C | $O_2$ | | 0 | 0 | 100 (**5**) |

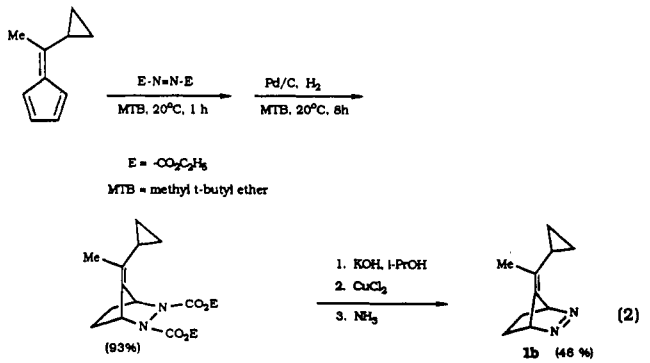
[a] Detected by capillary GC with *n*-nonane as standard. [b] Detected by capillary GC. Normalized to 100%; the deficit from 100% consists of unidentified volatile products. Error ca. 3% of the stated values. [c] The conversions were in all experiments 100% (azo test[10]), apart from entry 3, in which the conversion was 82%. [d] The trapping products are listed in brackets. [e] In the Rayonet photoreactor, except entry 9 in which the argon ion laser was used. [f] The argon ion laser was used.

ticular case T-**2b** under consideration, due to its special trimethylenemethane stability,[6] the cyclopropylcarbinyl rearrangement of this triplet diradical also should be kinetically less favorable than rearrangement of its singlet state, and consequently ring opening should not compete effectively with dimerization, despite its long triplet lifetime (ca. 1000 ns). This would constitute the first case for which the singlet rather than the triplet diradical undergoes cyclopropylcarbinyl rearrangement more readily.

Herein we present our results on the preparation of the cyclopropyl-substituted azoalkane **1b** and its thermolysis and photolysis in the absence and presence of diradical scavengers dioxygen ($^3O_2$) and 1,4-cyclohexadiene. Through careful product studies, we confirm that the singlet diradicals S-**2b** indeed affords cyclopropylcarbinyl rearrangement products, but the triplet diradical T-**2b** does not.

## Results

**Synthesis of the Azoalkane 1b.** The azoalkane **1b** was prepared in a manner analogous to **1a**[4] according to eq 2. The unsaturated




carbamate was synthesized through the addition of diethyl azodicarboxylate to the fulvene. Catalytic hydrogenation of the unsaturated carbamate led to the saturated carbamate, which on hydrolysis and oxidation afforded the azoalkane **1b** in a 54% overall yield. The azoalkane **1b** is labile and decomposes at temperatures above 35 °C.

**Thermolysis and Photolysis of the Azoalkane 1b under an Argon Gas Atmosphere.** The results are given in Table I. Thus, the thermolysis in solution (entry 1), the pyrolysis (entry 2), and the direct (entries 5–8) and the benzophenone-sensitized photolyses (entries 11 and 12) of the azoalkane **1b** under argon gas led to 2-methylbicyclo[4.3.0]nona-2,9-diene (**3**) and $C_{20}H_{28}$ dimers. The

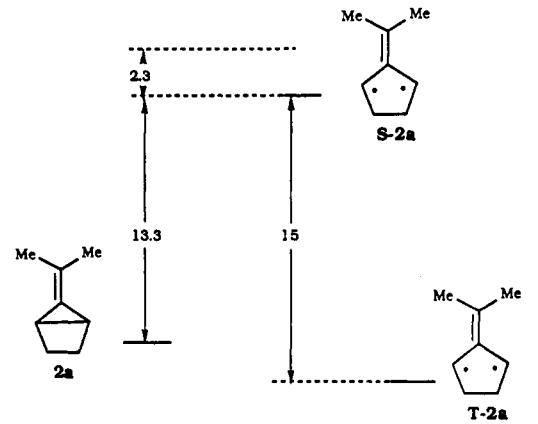


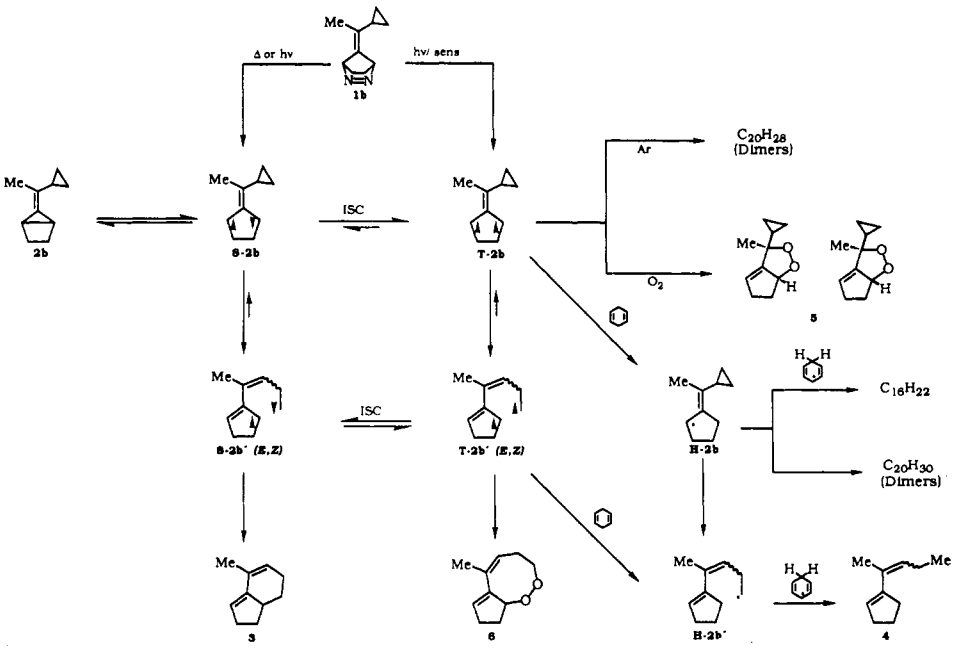

**Figure 1.** Energy diagram for the non-Kekulé diradicals S-**2a** and T-**2a**.

dimers could not be separated by preparative GC and were identified by GC–MS analysis ($m/z$ = 268). $^1H$ and $^{13}C$ NMR analysis showed that the dimer mixture possessed only intact cyclopropyl rings and no ring-opened units within the detection limits. The hydrocarbon **3** was isolated and fully characterized. At elevated temperature (10 °C), the direct photolysis led to increased amounts of the cyclopropylcarbinyl-rearranged hydrocarbon **3**. When the direct photolysis was carried out at −78 °C and monitored by NMR spectroscopy, besides the dimers, bicyclo[2.1.0]pentane **2b** was also observed. It was identified by comparison of its $^1H$ and $^{13}C$ NMR signals with those of the known bicyclo[2.1.0]pentane **2a**.[4b,d] Above −60 °C, the strained hydrocarbon **2b** decomposed exclusively into the dimers ($C_{20}H_{28}$); only traces of **3** could be detected by capillary GC. At the end of the Discussion section we shall offer a rationalization of this unusual mechanistic happenstance, which rests on the special trimethylenemethane stability[6] of the triplet diradical T-**2b**.

In the triplet-sensitized photolysis of the azoalkane **1b** at 6 °C (entry 11), only 2% of the rearranged hydrocarbon **3** was detected. For comparison, at a slightly higher temperature (10 °C), direct photolysis (entry 7) led to 13% of this rearrangement product.

**Thermolysis and Photolysis of the Azoalkane 1b in the Presence of 1,4-Cyclohexadiene.** The thermolysis of the azoalkane **1b** at 80 °C in a 0.1 M 1,4-cyclohexadiene solution (entry 3) led to the trapping product **4**, which was isolated by preparative GC together with the rearranged product **3**. Besides these, the $C_{20}H_{28}$ dimers and the $C_{20}H_{30}$ ($m/z$ = 270) dihydro dimers were also detected

**Scheme I.** Products and Reaction Pathways of the Singlet (S-**2b**) and Triplet Diradicals (T-**2b**)




by GC–MS analysis of the crude photolysate. Again, NMR analysis revealed that the dimers contained only intact cyclopropyl rings and no ring-opened units within the detection limits. Hydrocarbons with the molecular formula $C_{16}H_{22}$ ($m/z$ = 214) were also observed by GC–MS, which correspond to coupling products between the non-Kekulé diradical ($C_{10}H_{14}$) and the trapping agent 1,4-cyclohexadiene ($C_6H_8$). In the direct photolysis at 6 °C (entry 9), only 1% of the trapping product **4** was detected.

**Thermolysis and Photolysis of the Azoalkane 1b under Oxygen Gas.** While the benzophenone-sensitized photolysis (entry 12) of the azoalkane **1b** under 5 bar of oxygen gas led exclusively to the diastereomeric endoperoxides **5** in a 50:50 ratio, the direct photolysis (entry 10) also gave the rearranged hydrocarbon **3**. Both endoperoxides **5** were isolated by column chromatography and fully characterized. Of mechanistic significance is the fact that no dimers ($C_{20}H_{28}$) were formed under these conditions. In the thermolysis (entry 4) of the azoalkane **1b** at 60 °C under 5 bar of oxygen gas pressure, in addition to the rearranged hydrocarbon **3** and the diastereomeric endoperoxides **5** (ratio 50:50), a second endoperoxide **6** was isolated by column chromatography and fully characterized. The NMR data of peroxide **6** showed that it was the dioxygen trapping product of the cyclopropylcarbinyl ring-opened diradical.

## Discussion

Of the three modes of $N_2$ extrusion from azoalkane **1b** (Table I), namely, thermolysis (entries 1–4), direct photolysis (entries 5–10), and benzophenone-sensitized photolysis (entries 11 and 12), the process forming the most straightforward product composition is the latter mode. In view of its simpler nature, we shall begin our mechanistic discussion with this triplet-state process.

Under argon gas (Table I, entry 11), the triplet-state reaction almost exclusively afforded the dimers $C_{20}H_{28}$ and only traces of the rearranged hydrocarbon **3**. Thus at 6 °C the triplet diradical T-**2b** is reluctant to undergo cyclopropylcarbinyl ring opening to its rearranged congener T-**2b**′ (Scheme I); instead, a sufficiently high concentration (ca. micromolar) of T-**2b** builds up for dimerization into $C_{20}H_{28}$. This is analogous to the parent 2-isopropylidene-1,3-cyclopentanediyl (T-**2a**), for which exclusive dimerization was established.[4] Consequently, the activation barrier for cyclopropylcarbinyl rearrangement in T-**2b** is too high to compete with dimerization. In fact, when the $Ph_2CO$-sensitized photodenitrogenation of azoalkane **1b** was conducted under $O_2$ pressure (Table I, entry 12), even at 20 °C the endoperoxide **5** (no dimers $C_{20}H_{28}$ and rearranged hydrocarbon **3**) was produced exclusively with an intact cyclopropyl group. That no dimers $C_{20}H_{28}$ are observed derives from the fact that under the $O_2$ trapping conditions the $O_2$ concentration is at least millimolar, and thus dimerization cannot compete with trapping by $O_2$. More important for our mechanistic considerations, at room temperature the non-Kekulé triplet diradical T-**2b** does not undergo cyclopropylcarbinyl ring opening.

Next we shall take up the thermal denitrogenation of azoalkane **2b**. Although this mode furnishes the most complex product composition, it provides the most detailed insight into the behavior of the non-Kekulé diradicals under study. In the gas-phase pyrolysis (Table I, entry 2) at 160 °C/0.01 Torr and in the solution thermolysis (Table I, entry 1) at 80 °C under Ar gas, the major product was the rearranged hydrocarbon **3**, in addition to appreciable quantities of the dimer $C_{20}H_{28}$. The cyclopropylcarbinyl ring opening may have taken place at the singlet diradical S-**2b** stage (Scheme I), i.e., the pathway **1b** → S-**2b** → S-**2b**′ → **3**, or at the triplet diradical T-**2b** stage, i.e., **1b** → S-**2b** → T-**2b**′ → T-**2b**′ → S-**2b** → **3**. In view of the results for the triplet-sensitized denitrogenation of azoalkane **1b** (negligible cyclopropylcarbinyl ring opening), the latter more complex triplet route cannot also apply in the thermal extrusion of $N_2$ from **1b**. Instead, the cyclopropylcarbinyl rearrangement takes place in the singlet manifold, i.e., through the step S-**2b** → S-**2b**′ in Scheme I. The fact that in the gas-phase pyrolysis (Table I, entry 2) this ring opening gives a product distribution proportionally higher than in the solution thermolysis (Table I, entry 1) is clearly a temperature effect. At the higher temperature of the pyrolysis, cyclopropylcarbinyl rearrangement of S-**2b** competes more effectively with ISC to T-**2b** and subsequent dimerization.

A significant point concerns the regiochemistry of the cyclopropylcarbinyl ring-opening process S-**2b** → S-**2b**′ (Scheme I). Since there should be no preference for which lateral cyclopropylcarbinyl bond is cleaved, both the *Z* and *E* isomers of the ring-opened diradical S-**2b**′ must be expected; however, only the *Z* isomer can cyclize into tetrahydroindene **3**. The *E* isomer of S-**2b**′ is configurationally prohibited from cyclization into **3**, and its *E* → *Z* isomerization is not accessible on the time scale of ISC to T-**2b**′. Dimerization of the latter is not feasible because its lifetime, like that of the distonic triplet diradical **7**,[7] should be in the nanosecond range, and thus its concentration cannot build up sufficiently for such a bimolecular reaction. This is confirmed by the experimental fact that the $C_{20}H_{28}$ dimers possess only intact cyclopropyl groups. We postulate the reversible steps S-**2b** →

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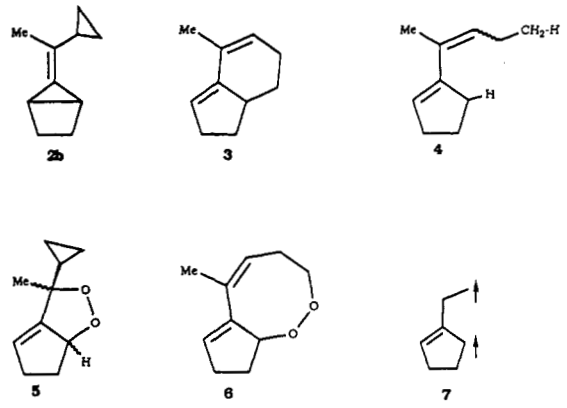


S-**2b**′ and T-**2b** → T-**2b**′ in Scheme I as a plausible route for eventual conversion of the *E* into the *Z* isomer of **2b**′ and the latter cyclization into the tetrahydroindene **3**. Unfortunately, at this point we have no experimental data to substantiate this mechanistic hypothesis.

The dioxygen trapping experiment under thermolysis conditions is revealing (Table I, entry 3). The endoperoxides **5** and **6**, which constitute trapping by $O_2$ of the diradicals S-**2b** (with intact cyclopropyl ring) and S-**2b**′ (cyclopropylcarbinyl ring opening), were the major products (together 75%), but substantial amounts (25%) of the rearranged hydrocarbon **3** were also formed. Again, no dimers $C_{20}H_{28}$ were observed, which implied that all T-**2b** triplets were trapped by $O_2$. At the lower temperature, 60 versus 80 °C (Table I, entries 1 and 3), it is reasonable that the cyclopropylcarbinyl ring opening S-**2b** → T-**2b**′ is less competitive with the intersystem-crossing process S-**2b** → T-**2b** (Scheme I).

The endoperoxide **5** (intact cyclopropyl group) derives mainly from $O_2$ trapping of the long-lived ($^3\tau$ = 916 ns for T-**2a**[5]) triplet diradical T-**2b**. The fact that no dimers $C_{20}H_{28}$ were observed, the characteristic products for the non-Kekulé triplet diradicals T-**2**, corroborates this supposition. However, in view of the relatively long singlet lifetime ($^1\tau$ = 0.28 ns[4b,e]) of the trimethylenemethane diradical S-**2a** ($^1\tau$ for S-**2b** should be very similar), some dioxygen trapping to afford intact endoperoxide **5** is feasible. After all, we showed that even the 10-fold shorter lived, localized singlet diradical 1,3-diphenyl-1,3-cyclopentanediyl ($^1\tau$ = 0.022 ns)[8] can be scavenged by $O_2$ to produce the corresponding stable endoperoxide. Nonetheless, the precursor for the rearranged endoperoxide **6** must be the cyclopropylcarbinyl ring-opened triplet diradical T-**2b**′ (Scheme I), because the corresponding singlet species S-**2b**′ should be too short-lived. Unfortunately, there exist no lifetime data of analogous derivatives for comparison;[3c] however, since the triplet lifetime of the 1,4-diradical **7** is only $^3\tau$ = 42 ns,[7] its singlet lifetime would be expected in the sub-picosecond range and thus is not amenable to dioxygen trapping, since such bimolecular processes are diffusion-controlled. Similarly, for the ring-opened singlet 1,6-diradical S-**2b**′ we expect a lifetime also in the sub-picosecond range. Consequently, the ISC process S-**2b**′ → T-**2b**′ competes with the cyclization S-**2b**′ → **3** to a sufficient degree that dioxygen trapping generates an appreciable quantity (7%) of observed rearranged endoperoxide **6** (Scheme I).

Similar conclusions were reached for the 1,4-cyclohexadiene trapping study in the thermolysis of azoalkane **1b** (Table I, entry 4), except that a more complex product composition was observed. Hydrogen abstraction requires a larger activation energy ($E_a$ ca. 5–7 kcal/mol)[9] than diffusion-controlled scavenging by $^3O_2$.[3a,c] The appreciable amounts (8%) of $C_{20}H_{28}$ dimer that are formed under these conditions are in support of the less effective scavenging by 1,4-cyclohexadiene versus dioxygen. As a trapping product, moderate quantities (12%) of the rearranged hydrocarbon **4** (double hydrogen abstraction from the 1,4-cyclohexadiene) was observed. Instead, the coupling products of the monoradical H-**2b** (single hydrogen abstraction from 1,4-cyclohexadiene), i.e., its dihydro dimer $C_{20}H_{30}$ (coupling of two H-**2b**) and cross dimer $C_{16}H_{22}$ (coupling of H-**2b** and $C_6H_7^{\bullet}$), prevail (Scheme I; Table I, entry 4). The fact that in these latter coupling products the cyclopropyl group is preserved (NMR evidence) underscores once again the reluctance of the non-Kekulé triplet species T-**2b** to ring-open into T-**2b**′. Thus, the principal route to the rearranged hydrocarbon **4** in the 1,4-cyclohexadiene trapping experiment should be the sequence S-**2b** → S-**2b**′ → T-**2b**′ → H-**2b**′ → **4**, but the cyclopropylcarbinyl rearrangement at the monoradical stage, i.e., H-**2b** → H-**2b**′, as a source for **4** cannot be neglected (Scheme I).

Finally, we take up the direct photolysis (Table I, entries 5–10), which embodies mechanistic features of both the triplet-sensitized and the thermal denitrogenations of azoalkane **1b**. Without delving into details, over the temperature range −78 to +25 °C (Table I, entries 5–8), the major route is dimer $C_{20}H_{28}$ formation through the ISC step S-**2b** → T-**2b** (Scheme I). This step is competed for by the cyclopropylcarbinyl rearrangement process S-**2b** → S-**2b**′ to afford the rearranged hydrocarbon **3**. In the presence of $O_2$, the $C_{20}H_{28}$ dimer is suppressed through formation of the endoperoxide **5** with an intact cyclopropyl group (Table I, entry 9). At the relatively low temperature (ca. 6 °C) of the direct photolysis mode, 1,4-cyclohexadiene is ineffective as a scavenger for T-**2b** because an insignificant amount (1%) of the rearranged hydrocarbon **4** is observed (Table I, entry 10).

From the temperature dependence on the product distribution of the direct photolysis of **1b**, i.e., with increasing temperature the proportion of cyclopropylcarbinyl rearrangement in the singlet diradical S-**2b** increases with respect to dimerization (Table I, entries 5–8), we estimate a difference in the activation barrier ($\Delta E_a$) between ISC (S-**2b** → T-**2b**) versus cyclopropylcarbinyl ring opening (S-**2b** → S-**2b**′) of ca. 2.8 ± 0.3 kcal/mol. Since as an entropy-controlled process ISC is usually temperature-independent,[10] we estimate that for this particular cyclopropylcarbinyl rearrangement in the singlet manifold (S-**2b** → S-**2b**′) the activating energy ($E_a$) is ca. 5 kcal/mol.

Experimental support for this mechanistic conclusion comes from the direct photolysis of **1b** at −78 °C (Table I, entry 5). At this low temperature the highly strained housane **2b** persists (confirmed by NMR), but on warming to room temperature, the dimer $C_{20}H_{28}$ prevails; only trace quantities (ca. 2%) of rearranged hydrocarbon **3** are produced. At the low temperatures of the warming-up process, the enthalpy-controlled cyclopropylcarbinyl ring opening cannot compete with the entropy-controlled ISC process and, thus, $C_{20}H_{28}$ dimer formation is essentially the exclusive product channel.

In summary, the cyclopropylcarbinyl radical probe enabled us to assess some additional mechanistic insight into the spin-selective reaction channels of the non-Kekulé singlet and triplet diradicals S-**2b** and T-**2b**. For comparison, the much studied[4] parent species S-**2a** and T-**2a** are more limited in their reaction alternatives. The singlet diradical S-**2a** may cyclize ($E_a$ ca. 2.3 kcal/mol[4b]) into the highly strained housane **2a**, but only below −53 °C because at higher temperatures it regenerates S-**2a** and intersystem-crosses to the ground-state triplet diradical T-**2a**. The latter has as its only option sufficient accumulation (micromolar concentration) for self-annihilation by dimer formation simply because the activation barrier for the reverse ISC process T-**2a** → S-**2a** is prohibitively large ($\Delta E_{ST}$ ca. 15 kcal/mol[4b]) to compete with dimerization at these temperatures.

All of the above transformations take place as well for the novel cyclopropyl-substituted derivatives S-**2b** and T-**2b**, but in addition, these diradicals have the choice of engaging in cyclopropylcarbinyl rearrangement ($E_a$ ca. 5 kcal/mol). What is unusual about the present case is that the latter rearrangement channel can, however, only be pursued at ambient temperatures (20–40 °C) by the much shorter lived singlet diradical S-**2b** ($^1\tau \approx$ 200–250 ps[11]), because

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(9) Hawari, J. A.; Engel, P. S.; Griller, D. *Int. J. Chem. Kinet.* **1987**, *17*, 1215.
(10) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978; p 187.

cyclopropylcarbinyl ring opening competes effectively with cyclization to its housane **2b** and ISC to its triplet species T-**2b**. Therefore, depending on the temperature, significant quantities of rearrangement products become detectable at the expense of dimerization.

On the other hand, the much longer lived triplet diradical T-**2b** ($^3\tau$ = 916 ns for T-**2a**[5]) is still destined to dimerize because cyclopropylcarbinyl rearrangement is too slow to compete with dimerization (<2 kcal/mol) unless much higher temperatures are used, i.e., >100 °C. Why is the triplet diradical T-**2b** reluctant to undergo cyclopropylcarbinyl ring opening? The special trimethylenemethane stability,[6] which provides for its unusually large triplet–singlet energy gap ($\Delta E_{ST}$ ca. 15 kcal/mol) and therewith ISC is too slow to compete with dimerization ($E_a$ < 2 kcal/mol), is presumably also responsible for the reluctance of cyclopropylcarbinyl rearrangement in the triplet diradical T-**2b**. By applying the facts known[4] about Berson's trimethylenemethane diradical **2a** to the present cyclopropyl-substituted case **2b**, the singlet species S-**2b** is expected to possess the perpendicular conformation, while the triplet state T-**2b** should be planar. The latter fact is to a large measure responsible for the special trimethylenemethane stability of the triplet non-Kekulé diradicals **2**. Thus, the S-**2b** diradical can be approximated in terms of two noninteracting allyl and cyclopropylcarbinyl radical centers, and thermochemical estimates suggest that ring opening to S-**2b** is exothermic by ca. 6 kcal/mol. It is, therefore, not surprising that the activation energy for the cyclopropylcarbinyl rearrangement of S-**2b** should be of the usual magnitude ($E_a$ ca. 5 kcal/mol).

In the ring-opened S-**2b** and T-**2b** distonic diradicals, however, the special trimethylenemethane stability no longer applies. Consequently, not only should their spin states be nearly isoenergetic they should also lie within the triplet–singlet energy gap of **2b** ($\Delta E_{ST}$ ca. 15 kcal/mol), i.e., ca. 6 kcal/mol below the S-**2b** and ca. 9 kcal/mol above the T-**2b** intact diradicals. Consequently, cyclopropylcarbinyl ring opening should be at least as much as ca. 14 kcal/mol (ca. 9 kcal/mol for the energy difference between T-**2b** and T-**2b**′ and ca. 5 kcal/mol for the normal activation energy of the ring-opening process T-**2b** → T-**2b**′) and cannot compete with dimerization ($E_a$ ca. 2 kcal/mol).[12]

The non-Kekulé triplet diradical T-**2b** is unusual in that it constitutes a "thermodynamic sink",[6] such that under the reaction conditions examined herein, it is kinetically protected from unimolecular processes such as ISC and cyclopropylcarbinyl rearrangement. Instead, it is destined to annihilate itself through dimerization by accumulating a sufficiently high (ca. micromolecular) concentration for such bimolecular reactions.

## Experimental Section

The IR spectra were taken on a Perkin-Elmer 1420 Infrared spectrometer in $CCl_4$. UV spectra were recorded on a Hitachi U-3200 spectrometer and mass spectra on a Varian MAT CH 7 mass spectrometer. The $^1H$ and $^{13}C$ NMR spectra were run on Bruker AW 80, AC 200, AC 250, and WM 400 instruments, with tetramethylsilane, deuteriodichloromethane, or deuteriochloroform as internal standards. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg, Würzburg, Germany. All melting points were taken on a Reichert Thermovar apparatus. Silica gel (60–230 mesh; Woelm) was used for the column chromatography. TLC analyses were run on silica gel foils, Polygram SIL $GC/UV_{254}$ (40 × 80 mm), from Macherey & Nagel. The photochemical reactions were carried out in a Rayonet RP-100 photochemical reactor equipped with 350-nm lamps. The 363.8-, 351.4-, 351.1-, 335.5-, and 333.6-nm UV lines of the Coherent INNOVA-100 argon ion laser were used in the laser photolyses. Gas chromatographic quantitative analyses were carried out on a Carlo Erba Strumentazione 4100 (FID). As an integrator, a Shimadzu C-R1B Chromatopac was used. 6-Cyclopropyl-6′-methylfulvene was prepared according to the literature procedure.[13]

**2,3-Dicarbethoxy-7-(2-cyclopropylpropylidene)-2,3-diazabicyclo[2.2.1]heptane.** To a solution of 4.00 g (30.2 mmol) of cyclopropylmethylfulvene in 50 mL of dry methyl *tert*-butyl ether was added at 20 °C a solution of diethyl azodicarboxylate (5.26 g, 30.2 mmol) in 20 mL of dry methyl *tert*-butyl ether. The resulting mixture was stirred for 1 h at 20 °C, and then 100 mg of Pd/C was added. The solution was degassed (20 °C/17 Torr) and vigorously stirred at 20 °C under a hydrogen gas atmosphere. After 12 h, removal of the catalyst by filtration and the solvent by distillation (30 °C/20 Torr) gave 8.52 g (91%) of a yellow, viscous oil, which could not be isolated in pure form either by column chromatography (silica gel, 1:4 petroleum ether/$Et_2O$) or by distillation 120 °C/0.01 Torr): IR ($CCl_4$) $\nu$ 3000, 1755, 1715, 1470, 1405, 1380, 1320, 1250, 1220, 1155, 1065, 915 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 0.20–0.40 (m, 4 H, cyclopropyl H), 0.95–1.10 (t, 6 H, $CH_3$), 1.20 (s, 3 H, $CH_3$), 1.25–1.35 (m, 1 H, cyclopropyl H), 1.52–1.80 (m, 4 H, 5-H and 6-H), 3.80–4.15 (m, 6 H, $OCH_2$, 1-H and 4-H); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 3.92 (t), 14.2 (q, $CH_3$), 14.3 (q, $CH_3$), 14.6 (d), 26.8 (t), 58.2 (d, C-1 or C-4), 59.0 (d, C-1 or C-4), 62.0 (t, $OCH_2$), 123.8 (s, C-7), 135.1 (s, C-8), 156.2 (s, CO).

**7-(2-Cyclopropylpropylidene)-2,3-diazabicyclo[2.2.1]hept-2-ene (1b).** A sample of 5.50 g (16.2 mmol) of the above carbamate was added to a solution of 5.00 g (97.2 mmol) of potassium hydroxide in 100 mL of *i*-PrOH and refluxed under nitrogen gas for 15 h. The reaction mixture was diluted with 100 mL of ice water, and concentrated HCl was added to adjust the pH to 1–2. With 12% $NH_3$ aqueous solution the pH was adjusted to 5–6, and 10 mL of a saturated $CuCl_2$ solution was added dropwise. The solution became dark and a brown solid precipitated. The solid was collected by filtration and subsequently dissolved in 50 mL of a 12% $NH_3$ solution. After 15 min, the $NH_3$ solution was extracted with $CH_2Cl_2$ (5 × 60 mL) and the combined organic layers were washed with 2 × 50 mL of $H_2O$, dried over $MgSO_4$, and concentrated by rotary evaporation (O °C/20 Torr). The crude product was purified by column chromatography (silica gel, 9:1 $CH_2Cl_2$/EtOAc, $R_f$ = 0.38) to produce 1.52 g (58%) of colorless pellets: mp 31–32 °C dec; IR ($CCl_4$) $\nu$ 3100, 3040, 3000, 2960, 2880, 1520, 1490, 1440, 1380, 1290, 1120, 1080, 1030 $cm^{-1}$; UV ($CH_3CN$) $\lambda_{max}$ (log $\epsilon$) 340 nm (2.264); $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 0.36–0.59 (m, 4 H, cyclopropyl H), 1.02 (d, $J$ = 7 Hz, 2 H, $H_{endo}$), 1.28 (s, 3 H, $CH_3$), 1.35–1.48 (m, 1 H, cyclopropyl H), 1.53–1.63 (m, 2 H, $H_{exo}$), 5.30 (d, $J$ = 2.5 Hz, 1 H, 1-H or 4-H), 5.49 (d, $J$ = 2.5 Hz, 1 H, 1-H or 4-H); $^{13}C$ NMR ($CDCl_3$, 63 MHz) $\delta$ 3.86 (t), 4.07 (t), 13.7 (q, $CH_3$), 14.4 (d), 21.3 (t, C-5, C-6), 73.4 (d, C-1 or C-4), 74.3 (d, C-1 or C-4), 123.7 (s, C-7), 138.9 (s, C-8); MS (70 eV) $m/z$ 162 (0.1) [$M^+ - N_2$], 134 (64) [$M^+ - N_2$], 119 (75), 105 (47), 91 (100). Anal. Calcd for $C_{10}H_{14}N_2$: C, 73.96; H, 8.70; N, 17.30. Found: C, 73.78, H, 8.93; N, 17.01.

**Thermolysis of the Azoalkane 1b in Benzene.** A solution of the azoalkane **1b** (30.0 mg, 0.185 mmol) in 3.00 mL of absolute benzene was heated to 80 °C for 1 h. After cooling, the reaction mixture was analyzed by capillary GC [30-m SE 30 fused silica capillary column, $N_2$ flow of 0.9 $kP/cm^2$; column temperature programmed at 60 °C (30 min) and then 10 °C/min up to 170 °C (40 min); injector and detector temperatures of 200 and 220 °C]. The product mixture consisted of 59% of 2-methylbicyclo[4.3.0]nona-2,9-diene (**3**), $t_R$(**3**) = 16.9 min, and 41% of eight higher molecular weight products, $t_R$ (dimers) = 56.0–60.8 min, which have a molecular ion peak at $m/z$ = 268 in the GC–MS.

**Dimers ($C_{20}H_{28}$)**: MS (70 eV) $m/z$ 267 (2) [$M^+$ + 1], 268 (19) [$M^+$], 135 (40), 134 (20), 133 (100), 119 (20), 105 (39), 93 (36), 91 (48), 81 (10), 79 (43), 77 (24), 67 (15), 65 (11), 55 (23), 53 (14), 44 (20), 41 (38), 39 (14).

**Flash Vacuum Thermolysis of the Azoalkane 1b.** The azoalkane **1b** (180 mg, 1.11 mmol) was sublimed (30 °C/0.01 Torr) through a 30 cm × 10 mm pyrolysis tube, which was heated at 160 °C. The thermolysate (138 mg (93%)) was collected in a liquid nitrogen cooled trap. The reaction mixture was than analyzed by capillary GC (for GC conditions, see above). The results are summarized in Table I. For analytically pure **3**, the sample was distilled three times (20–30 °C/0.01 Torr) to afford 85.0 mg (57%) of 2-methylbicyclo[4.3.0]nona-2,9-diene (**3**) as a colorless liquid.

**2-Methylbicyclo[4.3.0]nona-2,9-diene (3)**: IR ($CCl_4$) $\nu$ 2990, 2855, 1650, 1620, 1450, 1390, 1350, 1300, 1080, 1000, 820 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.21–1.43 (m, 2 H), 1.83 (s, 3 H, 10-H), 1.99–2.06 (m, 1 H), 2.14–2.24 (m, 3 H), 2.30–2.38 (m, 2 H), 2.60–2.66 (m, 1 H, 6-H), 5.52–5.58 (m, 2 H, 3-H and 9-H); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 18.9 (q, $CH_3$), 26.5 (t), 30.4 (t), 31.4 (t), 32.1 (t), 43.7 (d, C-6), 121.3 (d, C-3 or C-9), 126.6 (d, C-3 or C-9), 130.0 (s, C-1 or C-2), 144.7 (s, C-1 or C-2); MS (70 eV) $m/z$ 134 (72) [$M^+$], 119 (84), 105 (55), 91 (100), 77 (27), 65 (16), 51 (14), 41 (23), 39 (24). Anal. Calcd for

(11) (a) We assume here that the cyclopropyl-substituted diradicals S-**2b** and T-**2b** and the parent species S-**2a** and T-**2a** have similar activation energies for cyclization to the housanes, similar singlet-triplet energy gaps, and similar singlet and triplet lifetimes.

(12) We thank Prof. D. A. Dougherty for his enlightening comments on this point.

(13) Griesbeck, A. G.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Angew. Chem.* **1990**, *102*, 801.

$C_{10}H_{14}$: C, 89.48; H, 10.52. Found: C, 89.26; H, 10.38.

**General Procedure for the Direct Photolysis of the Azoalkane 1b.** A sample of 16.0–20.0 mg (0.100–0.123 mmol) **1b** in 3.00 mL of solvent ($CFCl_3$ or $C_6H_6$) was degassed and irradiated in the Rayonet photoreactor ($300 < \lambda < 370$ nm) at the appropriate temperature (−78 to +25 °C). After total conversion (negative azo test[14]), the photolysate was analyzed by capillary GC (for GC conditions, see above). The results are summarized in Table I.

**NMR Studies of the Direct Photolysate of the Azoalkane 1b at −78 °C.** A sample of 28.0 mg (0.173 mmol) of the azoalkane **1b** in 0.7 mL of $CFCl_3$ was processed according to the above general procedure. After total conversion (5 h, negative azo test), 0.1 mL of acetone-$d_6$ was added as a deuterium lock, and the $^1H$ and $^{13}C$ spectra were recorded at −78 °C. Besides the dimers, 5-(2-cyclopropylpropylidene)bicyclo[2.1.0]pentane (**2**) was identified as the main product by comparison with the known[4b,d] dimethyl derivate.

**5-(2-Cyclopropylpropylidene)bicyclo[2.1.0]pentane (2b)**: $^1H$ NMR ($CFCl_3$/acetone-$d_6$, −78 °C, 400 MHz) $\delta$ 0.40–0.58 (m, 4 H, cyclopropyl H), 1.58 (s, 3 H, $CH_3$), 2.05 (m, 2 H, 1-H and 4-H), 2.24 (m, 2 H, 2-$H_{exo}$ and 3-$H_{exo}$), the remaining resonances were not observed due to overlap with dimer signals; $^{13}C$ NMR ($CFCl_3$/acetone-$d_6$, −78 °C, 100 MHz) $\delta$ = 3.98, 4.45, 17.2, 20.8, 22.2, 22.3, 120.5, 126.4.

**Thermolysis of the Bicyclo[2.1.0]pentane 2b.** The photolysate was then allowed to warm up to −50 °C within 3 h, and the $^1H$ and $^{13}C$ spectra were recorded at this temperature; only the dimers were detected. Capillary GC analysis of the photolysate (for GC conditions, see above) confirmed that only dimers ($t_R$ = 56.0–60.8 min) were formed.

**Sensitized Photolysis of the Azoalkane 1b.** A sample of 21.4 mg (0.132 mmol) of the azoalkane **1b** and 10.0 mg (55.0 μmol) of benzophenone in 3.00 mL of benzene was dissolved, degassed, and irradiated at 6 °C with the 364-nm line of an argon ion laser (UV output 2.5 W). After total conversion [15 min (TLC, negative azo test)], the reaction mixture was analyzed by capillary GC (for GC conditions, see above). The results are summarized in Table I.

**Thermolysis of the Azoalkane 1b in the Presence of 1,4-Cyclohexadiene.** A sample of 9.50 mg (58.6 μmol) of **1b** and 500 mg (6.25 mmol) of 1,4-cyclohexadiene was degassed and heated at 80 °C for 5 h in a sealed ampule. After this time, the azoalkane was consumed (negative azo test), and capillary GC analysis gave the results shown in Table I. $C_{16}H_{22}$: GC–MS (70 eV) $m/z$ 215 (4) [$M^+$ + 1], 214 (12) [$M^+$], 143 (13), 136 (56), 121 (57), 107 (77), 93 (74), 91 (44), 79 (100), 77 (58), 69 (16), 65 (15), 55 (24), 53 (14), 43 (18), 41 (37), 39 (21), 29 (15), 27 (14). $C_{20}H_{30}$: GC–MS (70 eV) $m/z$ 271 (4) [$M^+$ + 1], 270 (20) [$M^+$], 228 (4), 227 (6), 137 (35), 136 (44), 135 (81), 134 (100), 119 (38), 107 (60), 93 (78), 91 (70), 81 (20), 79 (72), 77 (36), 67 (25), 65 (15), 55 (43), 43 (22), 41 (80), 39 (19), 29 (27), 28 (52), 27 (11).

For preparative purposes, the azoalkane **1b** (83.4 mg, 0.515 mmol) and 1.00 g (125 mmol) of 1,4-cyclohexadiene were dissolved in 5.00 mL of benzene, degassed, and heated at 80 °C for 8 h. After this time, the azoalkane was consumed (negative azo test). The 1-(2′-pent-2′-enyl)-cyclopentene (**4**) could be isolated together with hydrocarbon **3** by preparative GC (3-m, SE-30 column, $N_2$ flow of 2.0 kP/cm$^2$; oven, injector, and detector temperatures of 100, 150, and 180 °C; $t_R$(**3**) = 7.3 min and $t_R$(**4**) = 7.6 min). The yield of the 67:33 mixture of **3** and **4** was 26.4 mg (38%).

**1-(2′-Pent-2′-enyl)cyclopentene (4)**: $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 1.00 (t, $J$ = 7.5 Hz, 3 H, 5′-H), 1.58 (s, 3 H, 1′-H), 1.90–1.96 (m, 2 H, 4-H), 2.18–2.24 (m, 2 H, 4′-H), 2.40–2.47 (m, 4 H, 3-H and 5-H), 5.43 (t, $J$ = 7.5 Hz, 1 H, 2-H or 3′-H), 5.65–5.69 (m, 1 H, 2-H or 3′-H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 13.9 (q), 14.3 (q), 21.5 (t), 23.3 (t), 32.3 (t), 33.0 (t), 124.9 (d), 129.6 (d), 131.0 (s), 145.1 (s); MS (70 eV) $m/z$ 137 (6) [$M^+$ + 1], 136 (42) [$M^+$], 121 (45), 107 (52), 93 (100), 91 (41), 79 (72), 77 (40), 67 (50), 55 (27), 41 (48), 39 (41).

**Direct Photolysis of the Azoalkane 1b in the Presence of 1,4-Cyclohexadiene.** A mixture of 17.2 mg (0.106 mmol) of azoalkane **1b** and 160 mg (2.00 mmol) of 1,4-cyclohexadiene in 2.00 mL of absolute benzene was degassed and irradiated in the Rayonet photoreactor ($300 < \lambda < 370$ nm) at 6 °C. The reaction progress was monitored by TLC (azo test). After total consumption (4 h) of azoalkane **1b**, the reaction mixture was analyzed by capillary GC and GC–MS; the mass spectral data are described above. The results are summarized in Table I.

**Thermolysis of Azoalkane 1b under Oxygen Gas.** The azoalkane **1b** (100 mg, 0.617 mmol) was dissolved in 10.0 mL of absolute cyclohexane and heated to 60 °C under 5 atm of oxygen gas. The reaction progress was monitored by TLC (silica gel, $CH_2Cl_2$). After 2 h, the solvent was evaporated (20 °C/18 Torr), and subsequent flash chromatography (silica gel, $CH_2Cl_2$) yielded the following fractions: $R_f$ = 0.95, 15.2 mg (27%) of **3**; $R_f$ = 0.62, 47.1 mg (66%) of **5** (two diastereomers in a 50:50 ratio); $R_f$ = 0.49, 4.00 mg (7%) of **6**. In addition, 18.0 mg (18%) of unreacted starting material **1b** could be recovered.

**4-Cyclopropyl-4-methyl-2,3-dioxabicyclo[3.3.0]oct-5-ene (5)**: IR ($CCl_4$) $\nu$ 3090, 3020, 2945, 2865, 1620, 1440, 1370, 1175, 1110, 1050, 935, 830 cm$^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 0.26–0.57 (m, 8 H, cyclopropyl H), 1.02–1.21 (m, 2 H, cyclopropyl H), 1.28 (s, 3 H, $CH_3$), 1.47 (s, 3 H, $CH_3$), 1.79–1.90 (m, 2 H, 8-H), 2.08–2.19 (m, 2 H, 8-H), 2.73–2.86 (m, 4 H, 7-H), 5.28–5.38 (m, 2 H, 1-H), 5.46 (ddd, $J$ = 7.3, 1.7, 1.7 Hz, 1 H, 6-H), 5.57 (ddd, $J$ = 7.4, 1.3, 1.3 Hz, 1 H, 6-H); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 0.98 (t), 1.80 (t), 2.20 (t), 2.56 (t), 16.6 (d), 19.1 (d), 22.2 (q), 25.5 (q), 30.2 (t), 30.7 (t), 38.4 (t), 53.4 (t), 81.6 (s), 91.2 (d), 92.0 (d), 120.1 (d), 122.2 (d), 157.8 (s); MS (70 eV, $NH_3$) $m/z$ 201 (26) [$M^+$ + 35], 184 (100) [$M^+$ + 18], 167 (46) [$M^+$ + 1], 166 (4) [$M^+$], 149 (3), 134 (12), 133 (4), 119 (4). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.27; H, 8.49. Found: C, 72.55; H, 8.14.

**7-Methyl-2,3-dioxabicyclo[6.3.0]undecane-6,8-dione (6)**: IR ($CCl_4$) $\nu$ 3020, 2960, 2950, 1675, 1625, 1460, 1370, 1170, 1110, 1050, 920 cm$^{-1}$; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 0.81–0.85 (m, 1 H), 1.39 (s, 3 H, $CH_3$), 1.78–1.82 (m, 1 H), 2.14–2.18 (m, 1 H), 2.46 (m, 1 H), 2.68–2.74 (m, 2 H), 4.00–4.08 (m, 2 H, 4-H), 4.25–4.32 (m, 1 H, 1-H), 5.38–5.43 (m, 1 H, 6-H or 9-H), 5.59–5.65 (m, 1 H, 6-H or 9-H); $^{13}C$ NMR ($CDCl_3$, 63 MHz) $\delta$ 19.8 (q), 30.0 (t, C-11), 36.1 (t, C-5 or C-10), 37.6 (t, C-5 or C-10), 68.9 (t, C-4), 80.2 (d, C-1), 90.6 (d, C-6 or C-9), 123.2 (d, C-6 or C-9), the singlets at C-7 and C-8 could not be detected in the $^{13}C$ NMR spectra because of insufficient substance; MS (70 eV, $NH_3$) $m/z$ 201 (38) [$M^+$ + 35], 184 (53) [$M^+$ + 18], 167 (13) [$M^+$ + 1], 166 (13) [$M^+$], 154 (14), 144 (100), 142 (20), 137 (8), 127 (4), 119 (2), 109 (6), 96 (4). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.27; H, 8.49. Found: C, 72.53; H, 8.59.

**Direct Photolysis of the Azoalkane 1b under Oxygen Gas.** A 0.01 M solution of azoalkane **1b** in absolute cyclohexane (3.00 mL) was irradiated at 0 °C under 5 atm of oxygen gas with the 333-, 352-, and 364-nm lines of the argon ion laser (UV output 2.5 W). The progress of the reaction was monitored by TLC (silica gel, $CH_2Cl_2$) and by capillary GC (for GC, conditions see above). After total conversion, capillary GC analysis showed hydrocarbon **3** and the two diastereomeric peroxides **5** ($R_f$ = 34.7 and 36.0 min). The quantitative product studies are summarized in Table I.

**Sensitized Photolysis of the Azoalkane 1b under Oxygen Gas.** A 0.0167 M solution of **1b** and 0.0350 M of benzophenone in cyclohexane (2.00 mL) was irradiated with the 364-nm line of the argon ion laser (UV output 2.0 W) under 5 atm of oxygen gas at 20 °C. After total conversion (10 min), capillary GC analysis gave the results shown in Table I.

**Thermolysis of the Bicyclo[2.1.0]pentane 2b under Oxygen Gas.** A solution of 24.4 mg (0.163 mmol) of azoalkane **1b** in $CFCl_3$ (2.00 mL) was degassed by three freeze–pump–thaw cycles and was irradiated with the 333-, 352-, and 364-nm lines of the argon ion laser (UV output 2.0 W) at −78 °C under argon gas. After total conversion (1 h, negative azo test), the reaction mixture was allowed to warm up to 0 °C under 5 atm of oxygen gas. TLC analysis of the photolysate (silica gel, $CH_2Cl_2$) showed one spot ($R_f$ = 0.62), which exhibited a positive peroxide test. The quantitative product composition of the thermolysate was assessed by capillary GC (Table I).

**Thermolysis of the Peroxide 5 at 60 °C.** As a control experiment, 10.0 mg (60.2 μmol) of the two diastereomeric peroxides **5** was dissolved in absolute cyclohexane (1.00 mL) and heated at 60 °C for 1 h. TLC (silica gel, $CH_2Cl_2$) and capillary GC analyses showed that the two diastereomeric peroxides **5** were stable under these thermolysis conditions.

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