Pergamon

Tetrahedron Letters, Vol. 35, No. 15, pp. 2267-2270, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0305-H

The Lifetime of the 2,2-Dimethylcyclopentane-1,3-diyl Biradical by the Cyclopropylcarbinyl Radical Clock Method

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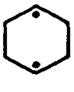
Abstract: The lifetime (τ) of the triplet 1-cyclopropylcyclopentane-1,3-diyl biradical (**6**) has been determined by the cyclopropylcarbinyl radical clock method to be 4 - 14 ns. This value is much longer than that of the norcyclopropyl analog **2** but is shorter than τ of the normethyl analog **5**. These results support the existence of the *gem*-dimethyl effect but bring into question the previously reported very short τ of **2**.

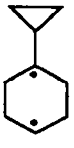
The structural features governing the lifetime (τ) of triplet 1,3-biradicals are currently under intensive scrutiny.[1-8] One of the largest effects on τ yet uncovered arises from the presence of *gem*-dimethyl groups on the carbon between the radical centers. For example, comparison of biradicals **1** and **2** reveals a decrease in triplet lifetime of at least 1000 fold.[6,8] The "*gem*-dimethyl effect" is seen in some other cyclopentane-1,3-diyls[3,6,8] but its magnitude is smaller.

Several years ago, we applied the cyclopropylcarbinyl (CPC) clock method to triplet 1,4-biradical **3**, whose lifetime was found by the O_2 trapping technique to be < 0.1 ns.[2] Our value[9] for **4** was much greater, 141 ns, indicating either that the O_2 trapping result on **3** was erroneous or that incorporation of the cyclopropyl group greatly lengthened τ. However, alkyl substitution on the radical centers in Norrish type II biradicals generally has very little effect on τ.[1]

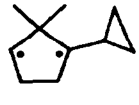

1
τ = 93 - 316 ns


2
< 0.1 ns


3
< 0.1 ns

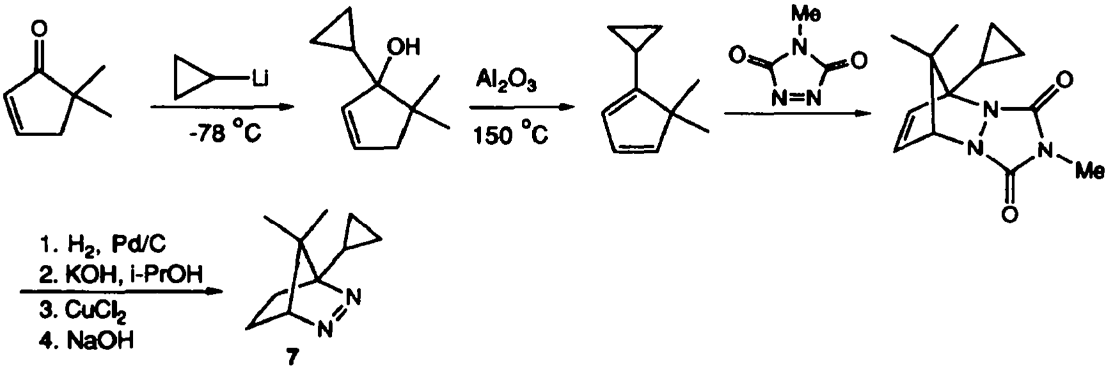

4
141 ns


5
59 ns


6
4 -14 ns

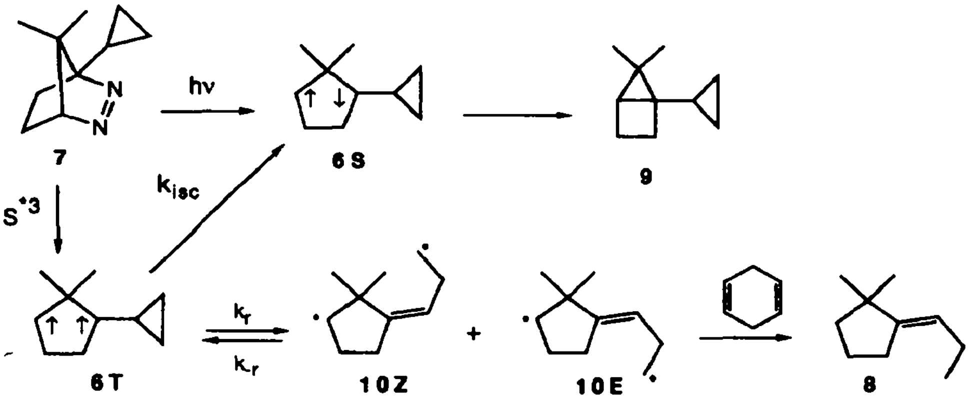
To check whether the cyclopropyl group increased τ in a well-studied biradical, we examined **5** and found that τ = 59 ns, based on a CPC rearrangement rate of 1.5×10^7 s^{-1} (see below).[4] This lifetime is *shorter* than that of the parent **1**, raising doubts about the exceedingly short τ of biradical **3** and, by analogy, of **2**. As an independent test of the dimethyl effect, we have now determined τ of biradical **6** by the CPC radical clock technique. Our conclusion is that τ of **6** lies between 4 and 14 ns, which is longer than the <0.1 ns originally reported[6,8] for **2**. However, the shorter τ of **6** than **5** supports the existence of the *gem*-dimethyl effect, which is still one of the largest known structural influences on triplet 1,3-biradical lifetimes.

One disadvantage of the CPC radical clock method is that the biradical precursor is not always easily synthesized. Nevertheless, bicyclic azoalkanes are such useful sources[10] of triplet 1,3-biradicals that we selected **7** as our synthetic target (cf. Scheme 1). Unlike the azoalkane precursor to normethyl biradical **5**, **7** is accessible as a single isomer by the Diels-Alder route because double bond migration in the *gem*-dimethyl cyclopentadiene is blocked. The spectra of **7** are as expected based on those of the previously reported normethyl analog.[4]



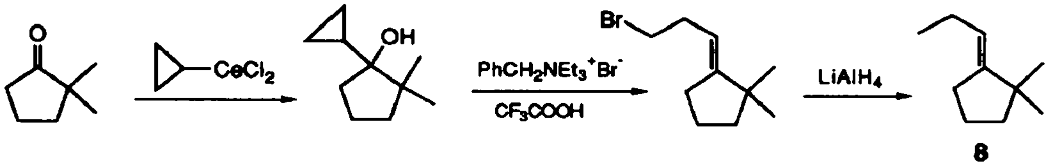
Scheme 1. Synthesis of Azoalkane 7

A degassed benzene solution of azoalkane **7**, triplet sensitizer (Michler's ketone) and a radical scavenger (1,4-cyclohexadiene, CHD) was irradiated at 366 nm where only the sensitizer absorbs light. Unlike our earlier study of normethyl **7**,[4] k_{isc} cannot be determined in the absence of a radical scavenger because the ring opened biradicals **10E, Z** (Scheme 2) would simply revert to **6**. Since the quantity of interest is the ratio of housane



Scheme 2. Reactions of Biradicals 6S (singlet) and 6T (triplet)

(9) to rearranged olefin (8), these values were determined by GC at various CHD concentrations. The NMR of authentic 9 was obtained by direct irradiation of 7 in C_6D_6 at 313 nm where 9 constituted 99.5% of the product. The identity of 8 was confirmed by GC coinjection on two different capillary columns with an authentic sample prepared as shown in Scheme 3. The E stereochemistry was verified by a NOE difference experiment. Each irradiated solution of 7 was assayed three times on two different GC columns with the following results: [CHD] (M), ratio 9/8: 0.70, 24.6; 1.48, 14.5; 2.95, 9.5. A kinetic analysis of Scheme 2 leads to equation (1) which implies that a plot of 9/8 versus 1/[CHD] will be linear with an intercept equal to the intersystem crossing rate over the rearrangement rate k_{isc}/k_r. The plot was indeed linear and fit the equation (9/8) = (14.1 ± 1.4)/[CHD] + (4.7 ± 0.8). If k_r is known, the intercept affords the desired k_{isc}.

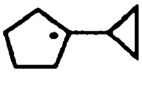


8

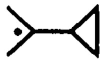
Scheme 3. Synthesis of Authentic Trapping Product 8

$$\frac{9}{8} = \frac{k_{isc}\,k_{-r}}{k_r\,k_t\,[\mathrm{CHD}]} + \frac{k_{isc}}{k_r} \qquad (1)$$

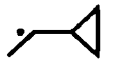
While our initial inclination was to take $k_r = 1.5 \times 10^7\ s^{-1}$, the value determined[4] for 11, a considerably faster k_r, $5.3 \times 10^7\ s^{-1}$, was reported for 12.[11, 12] However, k_r of 12 had earlier[13] been determined as $7 \times 10^6\ s^{-1}$ and the lower values fit better with the notion that increasing α-substitution should slow CPC rearrangement (k_r of 13 is $4.4 \times 10^7\ s^{-1}$ [13]). In the more recent work,[11] Tempo was assumed to trap 12 as fast as it trapped the smaller *tert*-butyl radical, yet a steric effect on Tempo trapping of 12 would result in a slower k_r. In view of these considerations, k_r of 6 is likely to be less than $5.3 \times 10^7\ s^{-1}$, so that k_{isc} is greater than $2.5 \times 10^8\ s^{-1}$ and τ is at least 4 ns.



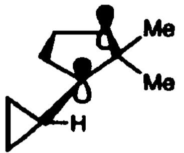
11



12



13



6a

It is conceivable that conformational effects cause the rearrangement rate of 6 to differ from that of 11 or 12. For example, the dimethyl group could force 6 into a conformation where the radical p orbital is aligned with one cyclopropyl ring bond, thus increasing k_r.[11] According to ESR spectroscopy, 12 exists in the "bisected" conformation where the dimethyl groups bisect the cyclopropane ring.[14] The same geometry is likely to hold for **11** and even **6** since the dimethyl groups do not interfere with the cyclopropane ring in conformation **6a**. Thus our estimate of $k_r < 5.3 \times 10^7$ s^{-1} is supported and the triplet lifetime of **6** is very likely to be > 4 ns. Based on the lifetime-shortening effect of cyclopropyl in **5** versus **1**, we would expect τ of **2** to exceed that of **6**. Therefore the reported value $\tau < 0.1$ ns for **2** is suspiciously short. On the other hand, the *gem*-dimethyl effect is real since applying the same k_r (1.5×10^7 s^{-1}) to both **5** and **6** gives $\tau = 59$ ns and 14 ns respectively.

Acknowledgment: Grateful acknowledgment is made to the National Science Foundation and the Robert A. Welch Foundation for financial support. We also thank Robert J. Edwards and Dr. Anne M. Culotta for exploratory work on the synthesis of **7**, and Professor R. Marshall Wilson for helpful discussion.

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(*Received in USA* 21 *December* 1993; *accepted* 3 *February* 1994)