UV-LASER PHOTOCHEMISTRY: NITROGEN EXTRUSION FROM THE AZOALKANE 4,5-DIAZATRI-CYCLOE4.4.0.0<sup>3</sup>.<sup>4</sup> JDEC-4-ENE. LIFETIME DETERMINATION OF BICYCLOE2.2.2JOCTA-2,5-DIYL BY DIOXYGEN TRAPPING.

## Waldemar ADAM' and Sven GRABOWSKI

Institute of Organic Chemistry, University of Würzburg, D-8700 Würzburg, F.R.G.

SUMMARY: The triplet lifetime of bicyclo[2.2.2]octa-2,5-diyl ( $\underline{5}$ ), generated by sensitized laser photolysis of 4,5-diazatwist-4-ene ( $\underline{6}$ ), was determined by dioxygen trapping. Therewith it constitutes the first localized, bicyclic triplet 1,4-diradical that could be trapped; despite its rigidity, it possesses a surprisingly short lifetime ( ${}^{3}\tau$  ca. 1 ns).

The short lifetime ( ${}^{3}\tau$  ca, 0.1 ns)<sup>1</sup>, of 1,4-cyclohexadiyl (<u>1a</u>) was attributed to the boat conformation (B) of this diradical (Fig. I), because this



Figure I Conformations of the 1,4-diradicals cyclohexadiyl <u>1a</u> and <u>5</u>, the latter obtained from MMPMI calculations<sup>7</sup>

conformation offers according to the "Salem rule"<sup>2</sup>' a favourable orientation of the radical lobes for intersystem crossing (ISC) by spin-orbit coupling. Substituting the radical sites with phenyl groups as in <u>1b,c</u> results a ca. 3000-fold increase in the triplet lifetimes [<sup>3</sup> $\tau$  (<u>1b</u>) = 275±15 ns; <sup>3</sup> $\tau$  (<u>1c</u>) =



365±20 ns]<sup>3</sup>, This was previously<sup>4</sup>, explained by postulating that benzyl stabilization of the radical centers relaxes the initial boat conformation (B) to the chair conformation (C) with parallel orientation of the radical lobes (Fig. I). This is unfavorable for ISC. Between the two extremes of the boat (B) and chair (C) conformations, a family of twistboat conformations exists, which can have skew-like orbital orientations (B') similar to the boat conformation (B) and thus fast ISC or parallel-like (C') similar to the chair conformation (C) with slow ISC. Moreover, theoretical work on tetramethylene<sup>4</sup>, predicts triplet ground states for these conformations with parallel orbital orienta6606

tions, i.e. the chair and twistboat conformations <u>C</u> and <u>C'</u>, respectively. In this context it is significant to note that exclusively the corresponding 1,5dienes and no bicyclo[2,2,0]hexanes are obtained from <u>16,c</u><sup>3</sup>'. Presumably the twistboat conformation <u>C'</u> or more likely the chair conformation <u>C</u> of these 1,4cyclohexadiyls serve as immediate precursors to products since the radical lobes are optimally aligned with the intervening 6-bond for ß-fragmentation but not for cyclization.

Triplet diradical  $2^{4}$ , offered the opportunity to explore the influence of the larger conformational space inherent with the flexibility of the seven-membered ring on the triplet lifetimes of 1,4-diradicals. The observed short lifetime for 2 (0.3  $\leq^{3} \tau \leq 3.3$  ns) suggested a conformation of this diradical of high ISC efficiency, e.g. similar to the boat or twistboat conformations <u>B</u> and <u>B'</u> in the 1,4-cyclohexadiyl series.

Even though MMPMI calculations<sup>7</sup>, provide great insight into such conformational rationalizations, in view of the inherent uncertainties concerning the conformations of flexible structures, experimental scrutiny seemed in order. Conformational flexibility can be circumvented by taking recourse to the more rigid bicyclic and even polycyclic diradical species, in which desired conformations can be frozen out at will. Such structural manipulation provides an excellent opportunity to study conformational effects on the ISC in diradicals with fixed geometries. Interesting information on the complexities of singlettriplet ISC in localized diradicals could be otained through lifetime measurements.

In view of Salem's orbital geometry rule it is thus not surprising that the bicyclic triplet 1,3-diradicals  $\underline{3}$  and  $\underline{4}$  were too short-lived ( ${}^{3}\tau$  < 0.1 ns) for trapping, because the interorbital angles of the radical lobes in  $\underline{3}$  and  $\underline{4}$  are  $\geq$  60°, i.e. efficient ISC. However, inspection of molecular models of the bicyclic 1,4-diradical  $\underline{5}$  suggests a widened angle between the radical lobes, as confirmed by MMPMI calculations on  $\underline{5}$  (Fig. I, interorbital angle  $\leq$  50°), but still hinting at a singlet ground state. To prove this prediction and to explore the effect of rigidity on ISC, dioxygen trapping of diradical  $\underline{5}$  was investigated.



Scheme I

The precursor to diradical 5, namely the azoalkane 4,5-diazatwist-4-ene ( $\underline{6}$ ), was known<sup>a</sup>). But its photolysis had not been studied. The photochemistry of the direct and benzophenone-sensitized irradiations in benzene is summarized in Scheme I and the yields recorded in Table I. Significant is the fact that the amount of cyclization product <u>7</u> obtained from <u>6</u> in both photolysis modes is considerable as compared to DBO<sup>5</sup>'. The chair conformation, optimal for Bscission, can not be reached in this rigid diradical. Hydrocarbon 7 was identified by comparison with the reported spectral data<sup>\*\*</sup>', and hydrocarbon <u>&</u> by coinjection with commercial available material. Since the bridgehead positions of azoalkane <u>6</u> bear no radical stabilizing substituents such as phenyl or vinyl groups, this DBO derivative is also quite "photoreluctant"<sup>5</sup>, Still more discouraging was the sensitized irradiation of <u>6</u> under oxygen pressure. Due to the low quantum yield for nitrogen loss, a quantitative study of dioxygen trapping's' was not possible. Performing this benzophenone-sensitized photolysis under 6 atm of oxygen, the hydroperoxide <u>9</u> (Scheme I) was isolated in 6% yield and characterized by reduction with Ph₃P to the known alcohol  $10^{9}$  . As expected on grounds of the geometry of diradical 5, exclusively the endo-isomer was found. An authentic sample of <u>10</u>°' confirmed this assignment.

Table I Product Yields (in %) of the Photolysis of Azoalkane <u>6</u>

Prod	uct	
Distribution"'		Conversion''
7	<u>8</u>	
67	33	10
73	27	З
	Prod Distrib <u>7</u> 67 73	Product Distribution"' <u>7 8</u> 67 33 73 27

a) in benzene at 8 °C;

b) GC peak area ratios normalized to total 100%;

c) determined by GC relative to azoalkane <u>6</u>; error limits ca. ± 2% of the stated values; mass balance > 95%;

d) argon ion laser.

Diradical 5 is therewith the first localized, bicyclic triplet diradical that could be trapped with molecular oxygen<sup>10</sup>. On the basis of the amount of trapping (6.4% at 6 atm  $O_2$ ) in the preparative experiment, we estimate<sup>1+</sup> a triplet lifetime of about 1 ns for diradical 5. Thus, despite the rigidity of the bicyclic skeleton; this diradical possesses a surprisingly short lifetime. Presumably a singlet ground state obtains. Furthermore, theoretical work<sup>4</sup> on the tetramethylene suggests, that sufficient flexibility remains in this bicyclic structure to reach triplet-singlet intersections via vibrational 6608

deformations, thereby providing for a short triplet lifetime. It should be of interest to make more rigid, localized diradicals with parallel orientation of the radical lobes. Which should exist as relatively long-lived triplet ground states in view of slow ISC.

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<sup>3</sup>r (ns) ~ 0.1 275±15 365±20 115±20 390±50 30000±4000

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