

# SINDO1 STUDY OF THE PHOTOCHEMICAL SYNTHESIS OF AZACYCLOBUTADIENE FROM 1,4-OXAZIN-2-ONE

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The mechanism of the photochemical decomposition of 1,4-oxazin-2-one to azacyclobutadiene and carbon dioxide was investigated by the semi-empirical MO method SINDO1. The relevant singlet and low-lying triplet potential energy hypersurfaces were studied and intermediates and transition structures were optimized with limited configuration interaction. The first step transforms 1,4-oxazin-2-one into a bicyclic lactone via internal cyclization. Then a stepwise bond breaking mechanism on the first excited triplet state yields azacyclobutadiene and CO<sub>2</sub>, whereas a reaction on the first excited singlet state is not common. It is shown that a simultaneous bond-breaking mechanism on the first excited singlet or on the first excited triplet is possible.

## INTRODUCTION

Azacyclobutadienes were initially stabilized by condensation with aromatic systems<sup>1</sup> or by donor groups.<sup>2</sup> Maier and Schäfer<sup>3,4</sup> have photochemically prepared unsubstituted azacyclobutadiene from 1,3-oxazin-6-ones, called azapyrones in a matrix. Irradiation with light of wavelength 288 nm (4.3 eV) transformed 1,3-oxazin-6-one in an argon matrix at 8 K into the bicyclic azalactone bicyclo[2.2.0]-3-aza-5-oxahex-2-en-6-one, called azadewarpyrone (Figure 1). Prolonged irradiation at the same wavelength led to photoelimination of CO<sub>2</sub>. Azacyclobutadiene could not be detected by IR spectroscopy. Only the fragmentation products HCN and acetylene were found in the matrix. Experiments with substituted 1,3-oxazin-6-ones resulted in differently substituted acetylenes and nitriles. From these facts, it was concluded that azacyclobutadiene occurs temporarily in the process. No mechanism was proposed. Semi-empirical calculations showed that during the photofragmentation of CO<sub>2</sub> (Figure 1) the C(1)—C(2) bond breaks first, then the C(5)—O(6) bond.<sup>5</sup> A simultaneous mechanism could be excluded. Similar results with respect to the mechanism were

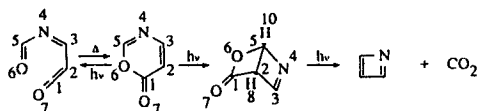


Figure 1. Experimental reaction scheme for 1,3-oxazin-6-one

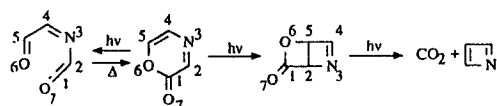


Figure 2. Reaction scheme for 1,4-oxazin-2-one

obtained in the quantum chemical investigation of the photoreaction of  $\alpha$ -pyrone.<sup>5</sup>

Analogous to 1,3-oxazin-6-one, a cyclization can convert 1,4-oxazin-2-one into a bicyclo[2.2.0]-5-aza-2-oxahex-5-en-3-one, called i-azadewarpyron in the following. Similarly to azadewarpyrone, i-azadewarpyrone represents a good photoprecursor of azacyclobutadiene. Figure 2 illustrates these reactions. Although the preparation of 1,4-oxazin-2-one has not yet been achieved, an investigation of the photoreaction is interesting, since the reaction mechanism can be compared with those of 1,3-oxazine-6-one and of  $\alpha$ -pyrone. All three substances are isoelectronic and therefore should show similar mechanisms for the photoreaction. In 1,4-oxazin-2-one, the C(1)—C(2) bond is polarized by the vicinal nitrogen N(3), which leads to a further weakening of this bond. Therefore, 1,4-oxazin-2-one should be a better photoprecursor than 1,3-oxazin-6-one for the formation of azacyclobutadiene.

## METHODS OF CALCULATION

The calculations were performed with the semi-empirical MO method SINDO1 with an extension to second- and third-row elements.<sup>6</sup> This method had

already been successfully applied to the photoisomerization of three- and five-membered rings, e.g. substituted diazirines,<sup>7</sup> cyclopentanone,<sup>8</sup> 2-methylfuran,<sup>9</sup> 2- and 3-cyanopyrrole,<sup>10</sup> thiophene,<sup>11</sup> tetrahydrothiophene<sup>12</sup> and tetramethylene sulphoxide.<sup>13</sup>

In the following, we denote the ground state by  $R_0$  and the vertically excited singlet states by  $R_1$ ,  $R_2$ , etc. Intermediates on the lowest singlet surface are denoted by  $I_1$  and  $I_1'$  and intermediates on the lowest triplet surface by  $^3I_1'$ . Minima including intermediates are characterized by exclusively positive roots of the force constant matrix, whereas transition structures have one negative root. Ground and excited equilibrium structures were optimized by a Newton-Raphson procedure. Bond lengths were optimized within 1% and bond angles and dihedral angles within  $1^\circ$ . Excited-state structures were optimized on their respective configuration interaction (CI) surfaces. Further details of the optimization procedure can be found in the furan treatment.<sup>9</sup> The size of configuration interaction was adjusted to guarantee an unambiguous qualitative explanation of the mechanism. Thus optimized points and vertical excitation energies were calculated with a  $278 \times 278$  CI, including single excitations from the eight highest OMOs to all 13 UMOs plus double excitations from HOMO/HOMO to UMO<sub>1</sub>/UMO<sub>2</sub> (UMO<sub>1</sub> stands for the three lowest UMOs and UMO<sub>2</sub> for all 13 UMOs). Valences were calculated with the valence criterion of Gopinathan and Jug.<sup>14,15</sup>

### 3. RESULTS AND DISCUSSION

#### Cyclization of 1,4-oxazin-2-one

From the calculated oscillator strengths in Table 1 it can be seen that the cyclization of 1,4-oxazin-2-one can occur via an excitation to the  $S_2$  or  $S_3$  state. The calculated bond valences (Table 2) of the excited states  $R_1$ ,  $R_2$  and  $R_3$  and the intermediates  $I_1$ ,  $I_2$ ,  $I_3$  and  $^3I_1$  show a significant decrease of valence  $V_{16}$  similarly to 1,3-oxazin-6-one. The breaking of the C(1)—O(6) bond

Table 1. Oscillator strengths and vertical excitation energies of 1,4-oxazin-6-one

Transition	Energy (eV)	Oscillator strength
$R_0 \rightarrow R_1$	3.95	$1.0 \times 10^{-3}$
$R_0 \rightarrow R_2$	4.73	$1.8 \times 10^{-2}$
$R_0 \rightarrow R_3$	4.83	$2.2 \times 10^{-2}$
$R_0 \rightarrow R_4$	5.02	$5.0 \times 10^{-3}$
$R_0 \rightarrow R_5$	5.36	$1.7 \times 10^{-2}$

leads to a ring opening. Then the generated  $\omega$ -azaketenal (Figure 2) can then react back to 1,4-oxazin-2-one in a thermally allowed fashion. In this way there is an analogy to 1,3-oxazin-6-one<sup>3,4</sup> (Figure 1) and  $\alpha$ -pyrone.<sup>16,17</sup> This pathway was not studied since it does not lead to azacyclobutadiene. The geometries of the stationary points involved in the cyclization are given in Table 3.

The reaction scheme of the cyclization is presented in Figure 3 and the potential energy curves in Figure 4. After excitation to the  $S_2$  or  $S_3$  state the transition to  $S_1$  occurs via IC and subsequently relaxation to  $I_1$ . In the  $S_1$  state cyclization to i-azadewarpyrone can take place. Starting from  $I_1$  the bond length  $r_{25}$  is shortened stepwise in the calculation under optimization of all other coordinates. At  $r_{25} = 2.1 \text{ \AA}$ , IC to the ground state occurs in the region of an avoided crossing. The barrier on the  $S_1$  surface is 1.03 eV. The cyclization can therefore take place only if the molecule can use its vibrational energy from the vertical excitation to overcome the barrier. The shape of the  $S_1$  potential curve is similar to those for the cyclization of  $\alpha$ -pyrone<sup>18</sup> and 1,3-oxazin-6-one.<sup>19</sup> Therefore, it can be concluded that the cyclization should be successful under similar experimental conditions, i.e. in an argon matrix under prolonged irradiation. A reaction in the  $T_1$  state is not very likely. Although the barrier of 1.24 eV is only slightly higher (Figure 5) than that on the  $S_1$  surface, the vibrational energy of the molecule would be dissipated to the environment in a matrix at low temperatures after ISC

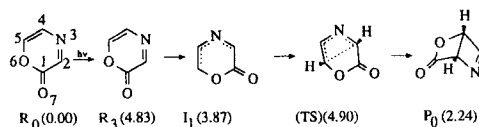
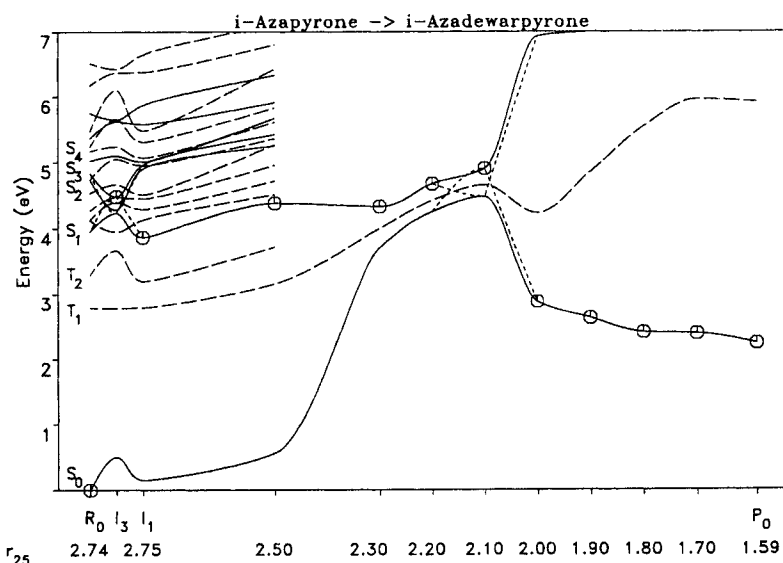
Table 2. Valences of reactant, intermediates and product of the cyclization of 1,4-oxazin-2-one

State	$V_{12}$	$V_{16}^a$	$V_{17}$	$V_{23}$	$V_{25}$	$V_{34}$	$V_{45}$	$V_{56}$
$R_0$ , $C_s$	0.964	0.966	1.854	1.853	0.075	1.068	1.777	1.055
$R_1$ , $C_s$	0.918	0.856	1.605	1.543	0.033	0.971	1.787	1.036
$R_2$ , $C_s$	0.900	0.827	1.742	1.767	0.033	1.101	1.332	1.053
$R_3$ , $C_s$	0.842	0.764	1.779	1.615	0.007	1.123	1.378	1.065
$I_1$	0.936	0.884	1.587	1.498	0.035	0.984	1.794	1.025
$I_2$	0.830	0.801	1.567	1.649	0.057	1.034	1.689	1.094
$I_3$	0.992	0.711	1.786	1.320	0.025	1.113	1.480	1.190
$^3I_1$	1.016	0.861	1.859	1.108	0.026	1.486	1.220	1.085
$P_0$	0.895	0.949	1.900	0.956	0.975	1.944	0.963	0.965

<sup>a</sup> relevant decreased values in italics

Table 3. Bond lengths  $r$  (Å), angles  $\alpha$  ( $^\circ$ ) and dihedral angles  $\phi$  ( $^\circ$ ) of reactant, intermediates and product of the cyclization of 1,4-oxazin-2-one

State	$r_{12}$	$r_{16}$	$r_{17}$	$r_{23}$	$r_{25}$	$r_{34}$	$r_{45}$	$r_{56}$
$R_0, C_s$	1.543	1.408	1.223	1.277	2.748	1.428	1.367	1.379
$I_1$	1.522	1.398	1.240	1.299	2.728	1.423	1.362	1.389
$I_2$	1.575	1.423	1.219	1.291	2.735	1.388	1.409	1.329
$I_3$	1.520	1.502	1.210	1.335	2.752	1.364	1.431	1.277
$^3I_1$	1.527	1.422	1.210	1.408	2.700	1.339	1.431	1.341
$P_0$	1.585	1.409	1.212	1.501	1.585	1.270	1.559	1.444
	$\alpha_{123}$	$\alpha_{234}$	$\alpha_{345}$	$\alpha_{456}$	$\alpha_{561}$	$\alpha_{217}$		
$R_0, C_s$	124.0	118.0	121.4	122.4	119.8	128.7		
$I_1$	122.7	118.6	120.1	124.3	117.4	122.1		
$I_2$	122.1	119.3	120.4	123.4	120.1	121.0		
$I_3$	124.0	118.4	121.7	122.6	121.5	131.3		
$^3I_1$	125.2	111.2	126.3	124.3	116.3	125.9		
$P_0$	116.9	91.7	100.1	117.3	92.3	139.0		
	$\phi_{1234}$	$\phi_{2345}$	$\phi_{2156}$	$\phi_{5617}$				
$R_0, C_s$	0.0	0.0	180.0	180.0				
$I_1$	-0.1	-0.3	179.4	-179.9				
$I_2$	-7.5	-4.4	167.7	-166.1				
$I_3$	0.9	0.1	179.3	-176.9				
$^3I_1$	0.0	-1.1	179.6	-179.8				
$P_0$	79.5	0.0	180.0	180.0				

Figure 3. Reaction scheme for the cyclization of 1,4-oxazin-2-one in the  $S_1$  stateFigure 4. Potential curve for the cyclization of 1,4-oxazin-2-one in the  $S_1$  state, with optimized points of geometry in circles

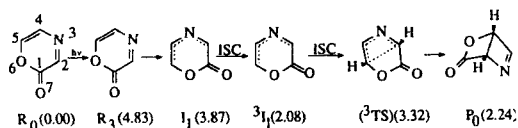


Figure 5. Reaction scheme for the cyclization of 1,4-oxazin-2-one in the  $T_1$  state

and a transition of the barrier would be impossible. This should not hold for a fast reaction in the  $S_1$  state, since the time-scale for IC is shorter than that for ISC.

### Stepwise bond breaking

The photoelimination of  $CO_2$  can start by excitation to the  $S_3$ ,  $S_4$  or  $S_5$  state. The calculated oscillator strengths and excitation energies are given in Table 4. The geometries of the stationary points involved in the reaction are presented in Table 5. Of the intermediates  $I_1$ ,  $I_2$  and  $I_3$  in the Franck–Condon zone, only  $I_3$  shows a significant decrease of valence  $V_{12}$  (Table 6).  $V_{12}$  is equally large for  $I_1$  as for  $R_0$ . The breaking of the C(1)—C(2) bond should therefore show a relatively high barrier. The valence  $V_{56}$  also shows no significant decrease. Therefore, breaking of the C(5)—O(6) bond is not to be expected. Figure 6 shows the reaction scheme of the

Table 4. Oscillator strengths and vertical excitation energies of i-azadewarpyrone

Transition	Energy (eV)	Oscillator strength
$S_0 \rightarrow R_1$	4.37	$4.0 \times 10^{-3}$
$R_0 \rightarrow R_2$	4.72	$2.0 \times 10^{-3}$
$R_0 \rightarrow R_3$	5.43	$8.0 \times 10^{-3}$
$R_0 \rightarrow R_4$	5.79	$2.3 \times 10^{-2}$
$R_0 \rightarrow R_5$	6.07	$1.0 \times 10^{-2}$

photofragmentation of i-azadewarpyrone starting in the  $S_1$  state and Figure 7 the corresponding potential curves. The reaction coordinate is the distance  $r_{12}$  until  $I_1'$ , then the distance  $r_{56}$ . All coordinates except the reaction coordinate were optimized. The stationary points were fully optimized.

In order to break the C(1)—C(2) bond, a barrier of 0.71 eV must be overcome on the  $S_1$  state surface. From  $r_{12} = 2.5 \text{ \AA}$  until  $I_1'$  ( $r_{12} = 2.998 \text{ \AA}$ ), IC to the ground state can occur favoured by an avoided crossing. Here the C(5)—O(6) bond breaks without barrier. In the  $T_1$  state there is no minimum in the Franck–Condon zone. Figure 8 shows the reaction scheme and Figure 9 the course of the fragmentation of

Table 5. Bond lengths  $r$  (Å), angles  $\alpha$  ( $^\circ$ ) and dihedral angles  $\phi$  ( $^\circ$ ) of reactant, intermediates and product of the photofragmentation of i-azadewarpyrone

State	$r_{12}$	$r_{16}$	$r_{17}$	$r_{23}$	$r_{24}$	$r_{25}$	$r_{34}$	$r_{45}$	$r_{56}$
$R_0$	1.585	1.409	1.212	1.501	1.995	1.588	1.270	1.559	1.444
$I_1$	1.589	1.403	1.206	1.459	2.295	1.594	1.349	1.553	1.435
$I_2$	1.595	1.402	1.227	1.546	2.064	1.557	1.257	1.568	1.441
$I_3$	1.604	1.470	1.201	1.489	2.050	1.612	1.278	1.544	1.391
$I_1'$	2.998	1.251	1.176	1.400	1.918	1.539	1.293	1.537	1.519
${}^3I_1'$	2.872	1.355	1.183	1.391	1.852	1.531	1.290	1.547	1.428
$P_0$	—	1.190	1.190	1.521	1.880	1.340	1.266	1.553	—
	$\alpha_{123}$	$\alpha_{234}$	$\alpha_{345}$	$\alpha_{456}$	$\alpha_{561}$	$\alpha_{217}$			
$R_0$	116.9	91.7	100.1	117.3	92.3	139.0			
$I_1$	115.3	109.6	80.5	120.8	94.0	137.5			
$I_2$	116.3	94.3	96.7	116.2	93.0	132.6			
$I_3$	118.5	95.3	97.3	118.9	95.7	142.8			
$I_1'$	116.4	90.7	98.3	116.5	124.6	105.3			
${}^3I_1'$	65.0	87.3	100.5	117.6	115.9	158.9			
$P_0$	—	84.3	98.3	—	—	—			
	$\phi_{1234}$	$\phi_{2345}$	$\phi_{2156}$	$\phi_{5617}$					
$R_0$	79.5	0.0	180.0	180.0					
$I_1$	78.1	-5.0	177.0	175.1					
$I_2$	80.4	-1.5	176.4	-163.6					
$I_3$	78.6	1.0	-179.4	178.1					
$I_1'$	52.6	-0.3	165.1	-9.5					
${}^3I_1'$	65.1	-9.5	176.5	-164.5					
$P_0$	—	0.0	—	—					

Table 6. Valences of reactant, intermediates and product of photofragmentation of *i*-azadewarpyrone

State	$V_{12}$	$V_{16}$	$V_{17}$	$V_{23}$	$V_{24}$	$V_{25}$	$V_{34}$	$V_{45}$	$V_{56}$
R <sub>0</sub>	0.895	0.949	1.900	0.956	0.024	0.975	1.944	0.963	0.965
R <sub>1</sub>	0.782	0.844	1.449	0.943	0.025	0.962	1.924	0.962	0.964
R <sub>2</sub>	0.890	0.938	1.880	0.729	0.054	0.950	1.327	0.794	0.945
R <sub>3</sub>	0.609	0.764	1.764	0.843	0.028	0.933	1.782	0.901	0.905
I <sub>1</sub>	0.894	0.951	1.889	0.842	0.033	0.814	1.157	0.859	0.944
I <sub>2</sub>	0.893	0.953	1.858	0.700	0.046	0.956	1.332	0.791	0.941
I <sub>3</sub>	0.580	0.678	1.891	0.824	0.025	0.785	1.800	0.922	0.973
I <sub>1</sub> '	0.021	1.476	2.090	1.110	0.150	0.903	1.672	0.970	0.546
<sup>3</sup> I <sub>1</sub> '	0.006	0.890	1.995	1.121	0.061	0.966	1.756	0.948	0.941
P <sub>0</sub>	—	1.872	1.872	0.921	0.055	1.919	1.915	0.947	—

*i*-azadewarpyrone in the T<sub>1</sub> state. After excitation to an excited singlet state, e.g. the S<sub>3</sub> state, the transition to the T<sub>1</sub> state takes place via IC and ISC. Here the breaking of the C(1)—C(2) bond occurs without barrier. At <sup>3</sup>I<sub>1</sub>' the molecule passes to the ground state via ISC. In the S<sub>0</sub> state the C(5)—O(6) bond can be broken by overcoming a barrier of 0.38 eV.

Calculations where the C(5)—O(6) bond is broken

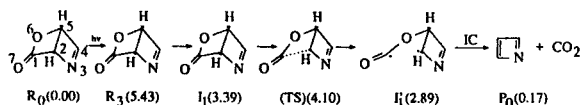


Figure 6. Reaction scheme for the C(1)—C(2) bond cleavage in the S<sub>1</sub> state; reaction to azacyclobutadiene via I<sub>1</sub>'

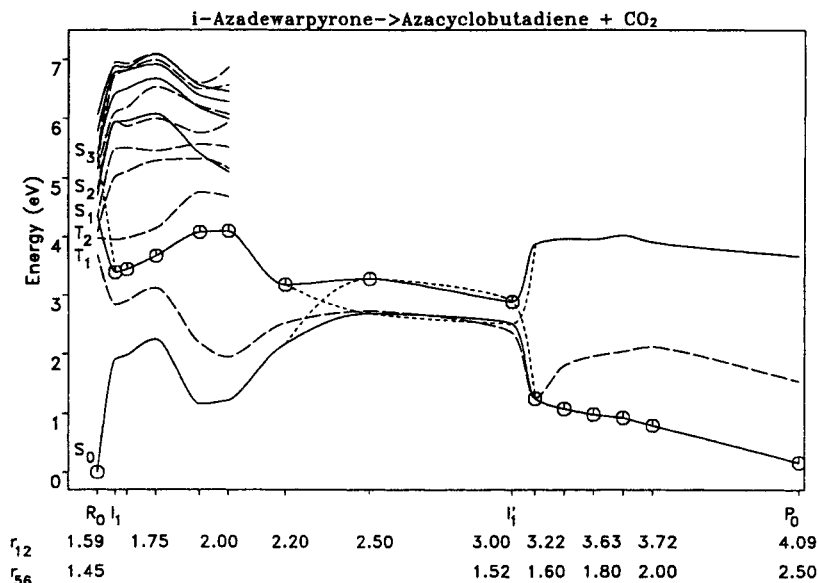


Figure 7. Potential curve of C(1)—C(2) bond cleavage in the S<sub>1</sub> state; reaction to azacyclobutadiene via I<sub>1</sub>', optimized points of geometry in circles

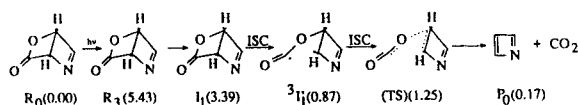


Figure 8. Reaction scheme for the C(1)—C(2) bond cleavage in the T<sub>1</sub> state; reaction to azacyclobutadiene via <sup>3</sup>I<sub>1</sub>'

first resulted in barriers of more than 3 eV in both the S<sub>1</sub> and T<sub>1</sub> states. Therefore, a primary breaking of the C(5)—O(6) bond can be excluded.

#### Simultaneous bond breaking

A simultaneous photoelimination of CO<sub>2</sub> is not very likely, because the valences  $V_{12}$  and  $V_{56}$  (Table 6) of the

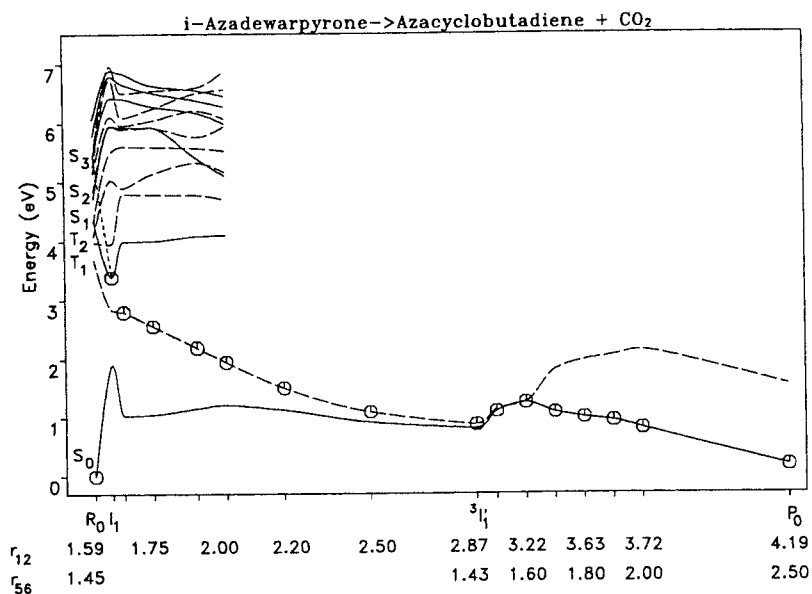


Figure 9. Potential curve for the C(1)—C(2) bond cleavage in the T<sub>1</sub> state; reaction to azacyclobutadiene via <sup>3</sup>I<sub>1</sub>, optimized points of geometry in circles

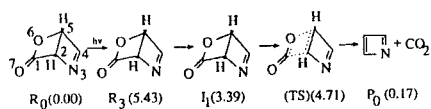


Figure 10. Reaction scheme for the simultaneous C(1)—C(2) and C(5)—O(6) bond cleavages in the S<sub>1</sub> state

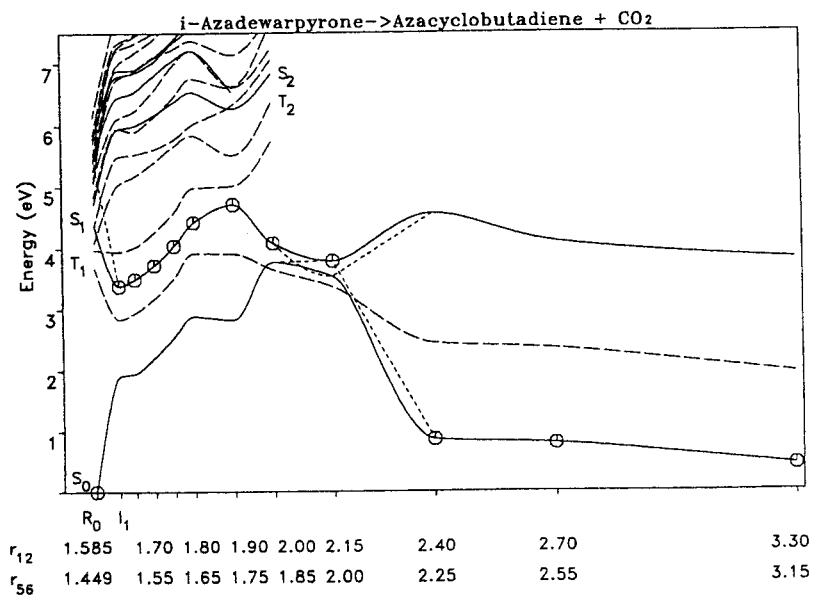


Figure 11. Potential curves for the simultaneous C(1)—C(2) and C(5)—O(6) bond cleavages in the S<sub>1</sub> state; optimized points of geometry in circles

excited states deviate very little from those of the ground state. As can be seen from Figure 10, the barrier for a reaction in the  $S_1$  state is 1.32 eV. Figure 11 shows the potential energy course of the reaction in the  $S_1$  state. After excitation to the  $S_3$  state, subsequent IC to the  $S_1$  state and relaxation to  $I_1$ , the system overcomes the barrier at  $r_{12} = 1.9 \text{ \AA}$  and  $r_{56} = 1.75 \text{ \AA}$ . At  $r_{12} = 2.15 \text{ \AA}$  and  $r_{56} = 2.6 \text{ \AA}$  IC to the ground state in the region of an avoided crossing takes place. In the  $S_0$  state the system relaxes to  $P_0$ . The reaction coordinates are the distances  $r_{12}$  and  $r_{56}$ . Starting from  $R_0$  a linear interpolation to the two separated molecules  $\text{CO}_2$  and azacyclobutadiene at distances  $r_{12} = 3.30 \text{ \AA}$  and  $r_{56} = 3.15 \text{ \AA}$  was performed. Subsequently these points were optimized except for the reaction coordinates  $r_{12}$  and  $r_{56}$ . The simultaneous photoelimination in the  $T_1$  state shows a similarly high barrier (Figures 12 and 13). The reaction coordinate in Figure 12 is the same as that in Figure 10. Since both reactions show barriers of more than 1 eV, a simultaneous bond breaking is not possible.

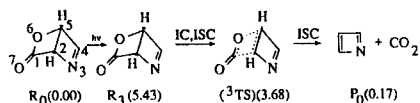


Figure 12. Reaction scheme for the simultaneous C(1)—C(2) and C(5)—O(6) bond cleavages in the  $T_1$  state

## CONCLUSION

The results indicate that *i*-azadewarpyrone yields azacyclobutadiene via a stepwise mechanism, whereas the simultaneous fragmentation in the  $S_1$  and  $T_1$  states can be excluded because of the high barriers. For the stepwise mechanism the reaction in the  $T_1$  state is favoured, because there is no barrier with respect to C(1)—C(2) bond breaking. The subsequent small barrier of 0.38 eV on the ground-state surface should be overcome in a matrix even at temperatures below 100 K. A reaction in the  $S_1$  state is unlikely because of the relatively high barrier of 0.71 eV. Compared with 1,3-oxazin-6-one,<sup>19</sup> 1,4-oxazin-2-one, represents a better photoprecursor to azacyclobutadiene, because the breaking of the C(1)—C(2) bond takes place without barrier in this case. This should increase the quantum yield substantially, which makes a prolonged irradiation unnecessary. This should reduce or prevent secondary photofragmentation of azacyclobutadiene and allow a spectroscopic measurement of this compound.

## ACKNOWLEDGEMENTS

The calculations were performed on the CYBER 180/995 and Siemens S400/40 computers at Universität Hannover. F. Neumann thanks the Konrad-Adenauer-Stiftung for a predoctoral fellowship.

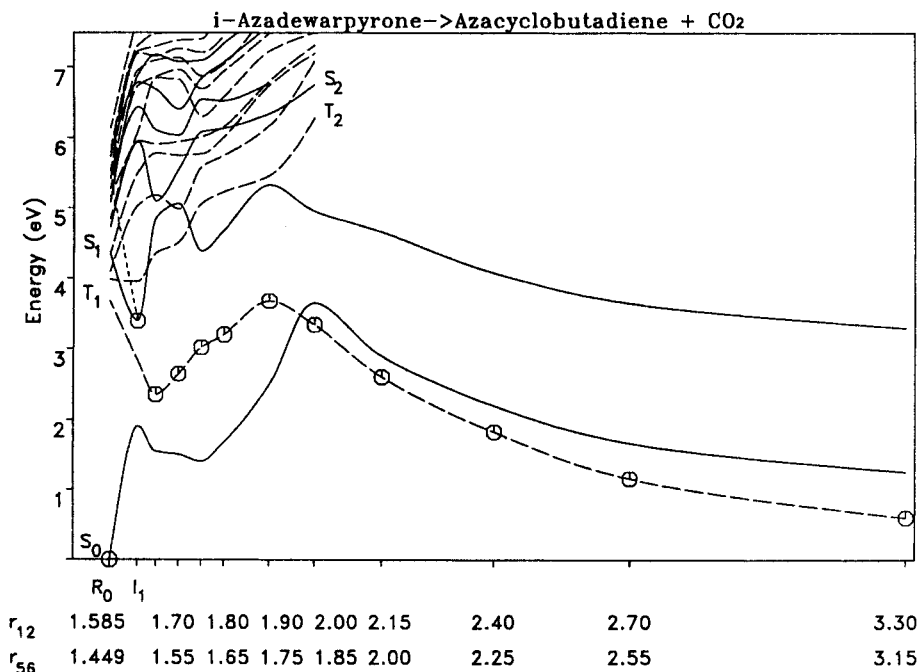


Figure 13. Potential curves for the simultaneous C(1)—C(2) and C(5)—O(6) bond cleavages in the  $T_1$  state; optimized points of geometry in circles

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