SINDO1 Study of Photochemical Synthesis of Azacyclobutadiene from 1,3-Oxazin-6-one

Frank Neumann and Karl Jug*

Theoretische Chemie, Universität Hannover, Am Kleinen Felde 30, 30167 Hannover, Germany

Received March 4, 1994 (Revised Manuscript Received August 9, 1994®)

SINDO1 calculations were performed on the photochemical reaction of 1,3-oxazin-6-one to azacyclobutadiene and carbon dioxide. The mechanism was compared with the corresponding reaction for cyclobutadiene and found to be similar. Again the first step transforms 1,3-oxazin-6-one into a bicyclic lactone via internal cyclization. Then a stepwise bond breaking mechanism on the first excited singlet state yields azacyclobutadiene and CO_2, whereas a simultaneous bond breaking mechanism is not possible. In addition, a rearrangement of the bicyclic lactone on the first excited triplet surface leads to tricyclo[2.1.1.$0^{5,6}$]-5-aza-3-oxahexan-2-one.

1. Introduction

The first azacyclobutadienes were stabilized by condensation with aromatic systems[1] or by donor groups.[2] At that time there was no information about unsubstituted azacyclobutadiene. Maier and Schäfer[3,4] have photochemically prepared azacyclobutadiene in a matrix starting from 1,3-oxazin-6-ones, also called azapyrones. For irradiation at 254 nm (4.9 eV) it could be shown that a ring opening of the 1,3-oxazin-6-one to ω-4-azaketenal (Figure 1) is possible as in the case of the isoelectronic α-pyrone.[5,6] The thermally induced ring closure of the photochemical opening of the ring occurred here also at the low temperatures of liquid nitrogen. Irradiation of the 1,3-oxazin-6-one at 288 nm (4.3 eV) in an argon matrix at 8 K led to the bicyclic azalactone bicyclo[2.2.0]-3-aza-5-oxahex-2-en-6-one, also known as azadewarpyrone. Long irradiation times at the same wavelength led to the photoelimination of CO_2. 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. It was concluded that azacyclobutadiene would occur as an intermediate in the process. However, no mechanism could be presented.

In this paper we want to elucidate the reaction mechanism and to compare it to the corresponding mechanism for the formation of cyclobutadiene. In particular, the feasibility of formation and the question of the experimental elusiveness of azacyclobutadiene in this reaction is discussed.

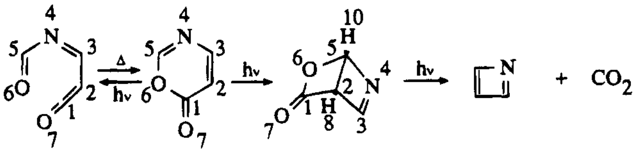

Figure 1. Experimental reaction scheme of 1,3-oxazin-6-one.

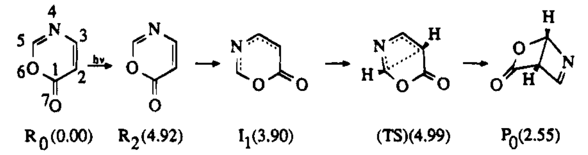

Figure 2. Reaction scheme of the cyclization of 1,3-oxazin-6-one in the S_1 state.

Table 1. Calculated Vertical Excitation Energies (eV) and Oscillator Strengths of 1,3-Oxazin-6-one

transition	excitation energy (eV)	oscillator strength
$R_0 \rightarrow R_1$	4.64	1.0×10^{-3}
$R_0 \rightarrow R_2$	4.92	2.1×10^{-2}
$R_0 \rightarrow R_3$	5.08	2.6×10^{-2}
$R_0 \rightarrow R_4$	5.70	5.0×10^{-3}
$R_0 \rightarrow R_5$	5.86	1.0×10^{-3}

2. Results and Discussion

The method of calculation is described in the preceding paper.[7] Energies and properties of optimized structures were determined with a 278 × 278 CI. Here all single excitations from the eight highest occupied MOs (OMOs) in all 13 unoccupied MOs (UMOs) were considered. In addition, all double excitations of the type HOMO/HOMO → UMO_1/UMO_2 were included. UMO_1 denotes the three lowest UMOs, UMO_2 all UMOs. This was necessary for a consistent CI because of topological crossing of the three lowest UMOs during the reaction.

The geometries are optimized on the potential surfaces relevant for the reaction. These points are marked with circles. All other states of these geometries are calculated by configuration interaction. The presentation of the figures follows that of the preceding paper.[7]

2.1. Cyclization of 1,3-Oxazin-6-one. The cyclization reaction starts with an excitation in the second or third excited singlet state, because the other calculated transitions represent only very weak bands (Table 1). Subsequently, internal conversion (IC) to the S_1 state occurs via avoided crossings. The intermediate I_3, I_2, and $^3I_1$ are almost planar (Table 2). In I_1 the $O^{(6)}-C^{(1)}-O^{(7)}$ group is rotated out of the ring plane. The hydrogen atoms $H^{(8)}$ and $H^{(10)}$ stand out of the ring plane. The weakest bond in the three lowest vertically excited states R_1, R_2, R_3 (Table 3) is that of $C^{(1)}-O^{(6)}$. This bond is even weaker in I_2 and I_3. If this bond breaks, ω-4-azaketenal

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® Abstract published in *Advance ACS Abstracts*, September 15, 1994.

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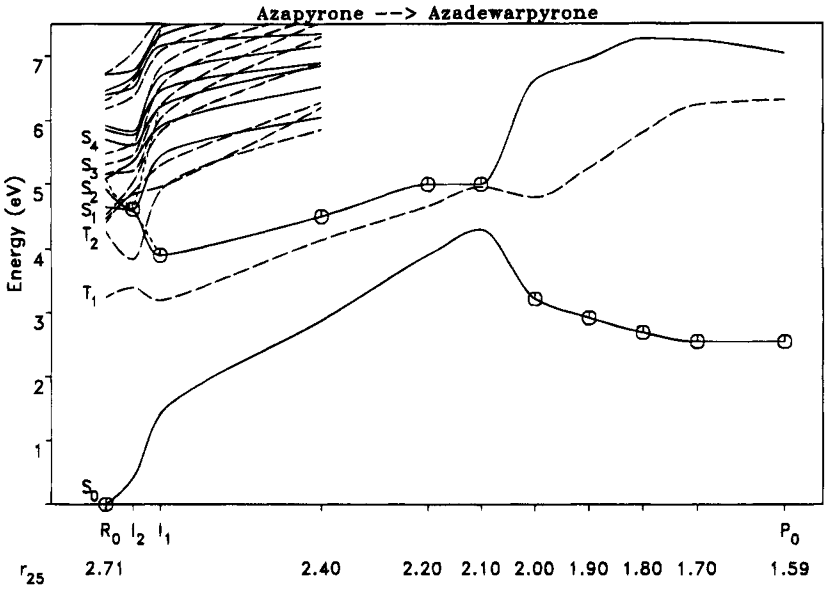

Figure 3. Potential curves for the cyclization of 1,3-oxazin-6-one in the S_1 state, optimized points of geometry (○).

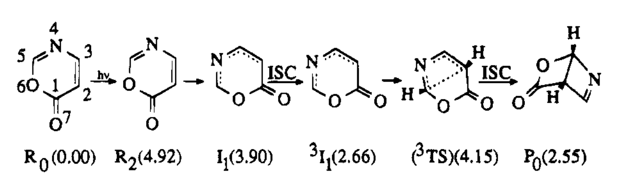

Figure 4. Reaction scheme of the cyclization of 1,3-oxazin-6-one in the T_1 state.

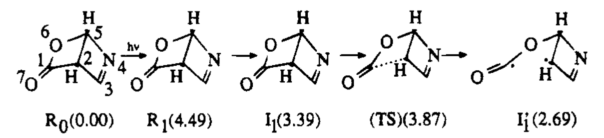

Figure 5. Reaction scheme for $C^{(1)}-C^{(2)}$ bond breaking in the S_1 state; reaction to I'_1.

Table 2. Bond Lengths r (Å), Bond Angles α (deg), and Dihedral Angles ϕ (deg) of Reactant, Intermediate, and Product of the Cyclization of 1,3-Oxazin-6-one

state	r_{12}	r_{16}	r_{17}	r_{23}	r_{25}	r_{34}	r_{45}	r_{56}
R_0, C_s	1.515	1.424	1.221	1.364	2.709	1.412	1.287	1.348
I_1	1.507	1.477	1.210	1.445	2.714	1.313	1.376	1.319
I_2	1.530	1.484	1.210	1.437	2.519	1.330	1.345	1.281
I_3	1.526	1.460	1.214	1.399	2.700	1.356	1.320	1.300
$^3I_1$	1.527	1.408	1.221	1.499	2.732	1.392	1.286	1.366
P_0, C_1	1.578	1.402	1.212	1.542	1.591	1.271	1.493	1.444

state	α_{123}	α_{234}	α_{345}	α_{456}	α_{561}	α_{217}
R_0, C_s	118.7	123.9	114.6	129.4	119.8	131.1
I_1	118.3	124.6	114.9	125.3	118.6	132.3
I_2	118.1	124.4	115.2	129.9	121.2	133.3
I_3	118.1	124.0	115.1	130.7	119.2	131.1
$^3I_1$	116.2	121.6	115.4	130.8	119.4	127.8
I_0	114.9	102.3	89.7	116.4	92.2	137.4

state	ϕ_{1234}	ϕ_{2345}	ϕ_{2156}	ϕ_{5617}	ϕ_{4328}	ϕ_{34510}
R_0, C_s	0.0	0.0	180.0	180.0	180.0	180.0
I_1	*−3.5*	*−4.8*	*−159.9*	*−156.3*	*−158.2*	*129.9*
I_2	*−5.3*	*3.0*	178.9	178.0	177.8	179.0
I_3	*−2.9*	*0.7*	178.6	178.8	179.7	180.1
$^3I_1$	*−8.0*	*−3.6*	172.7	174.4	−175.4	−172.1
P_0	−72.4	−0.9	−178.3	−176.7	129.5	−129.4

(Figure 1) as mentioned in the introduction is formed. The reaction is reversible and was not investigated here. In the course of irradiation a photochemical equilibrium between 1,3-oxazin-6-one and azadewarpyrone[3,4] is formed. Figure 2 shows the reaction scheme of the cyclization reaction on the S_1 potential surface and Figure 3 shows the corresponding potential curves.

Table 3. Valencies of Reactant, Intermediate, and Product of the Cyclization of 1,3-Oxazin-6-one

state	V_{12}	V_{16}	V_{17}	V_{23}	V_{25}	V_{34}	V_{45}	V_{56}
R_0, C_s	1.013	0.867	1.855	1.778	0.067	1.095	1.712	1.114
R_1, C_s	0.925	*0.771*	1.423	1.762	0.061	1.066	1.723	1.098
R_2, C_s	0.928	*0.722*	1.743	1.443	0.008	1.206	1.349	1.113
R_3, C_s	0.814	*0.744*	1.650	1.538	0.030	1.135	1.509	1.141
I_1	0.996	*0.623*	1.889	1.206	0.047	1.530	1.093	1.270
I_2	0.968	*0.630*	1.828	1.217	0.035	1.447	1.160	1.268
I_3	0.925	0.723	1.458	1.657	0.067	1.161	1.563	1.187
$^3I_1$	1.016	0.877	1.830	0.987	0.011	1.188	1.614	1.066
P_0	0.893	0.965	1.889	0.973	0.957	1.922	0.955	0.944

Table 4. Calculated Vertical Excitation Energies (eV) and Oscillator Strengths of Azadewarpyrone

transition	excitation energy (eV)	oscillator strength
$R_0 \rightarrow R_1$	4.49	3.0×10^{-3}
$R_0 \rightarrow R_2$	4.79	1.0×10^{-3}
$R_0 \rightarrow R_3$	5.41	6.0×10^{-3}
$R_0 \rightarrow R_4$	5.84	2.7×10^{-2}
$R_0 \rightarrow R_5$	6.05	1.3×10^{-2}

Table 5. Bond Lengths r (Å) and Bond Angles α (deg) of Reactant, Intermediates, and Products of the Photoreaction of Azadewarpyrone

state	r_{12}	r_{13}	r_{16}	r_{17}	r_{23}	r_{24}	r_{25}	r_{34}	r_{45}	r_{56}
R_0	1.515	2.630	1.402	1.212	1.542	2.197	1.591	1.271	1.493	1.444
I_1	1.588	2.661	1.408	1.211	1.509	1.901	1.627	1.363	1.464	1.413
$^3I_1$	1.579	2.603	1.406	1.208	1.540	2.215	1.573	1.417	1.486	1.429
I'_1	2.953	3.631	1.335	1.179	1.384	*1.743*	1.520	1.376	1.440	1.444
$^3I'_1$	2.961	3.318	1.386	1.183	1.457	*1.978*	1.526	1.286	1.499	1.401
I'_0	2.844	3.413	1.379	1.181	1.464	*1.975*	1.528	1.281	1.503	1.404
P_{0a}			1.190	1.190	1.553	2.141	1.340	1.266	1.521	
P_{0b}	2.502	1.574	1.411	1.215	1.527	1.423	1.527	1.500	1.480	1.436

state	α_{123}	α_{234}	α_{345}	α_{456}	α_{561}	α_{217}
R_0	114.9	102.3	89.7	116.4	92.2	137.4
I_1	118.5	82.7	107.6	120.0	91.5	136.7
$^3I_1$	113.1	96.9	88.7	119.6	92.2	139.0
I'_1	108.1	*78.3*	*103.8*	118.2	116.8	157.0
$^3I'_1$	90.8	*92.1*	*95.3*	117.2	120.5	150.2
I'_0	99.8	*91.8*	*95.3*	114.7	118.7	166.9
P_{0a}		98.3	84.3			
P_{0b}	90.0	90.0	90.0			

The reaction coordinate in Figure 3 is the distance r_{25} of the $C^{(2)}-C^{(5)}$ bond. The bond length is successively shortened under optimization of all other coordinates. At

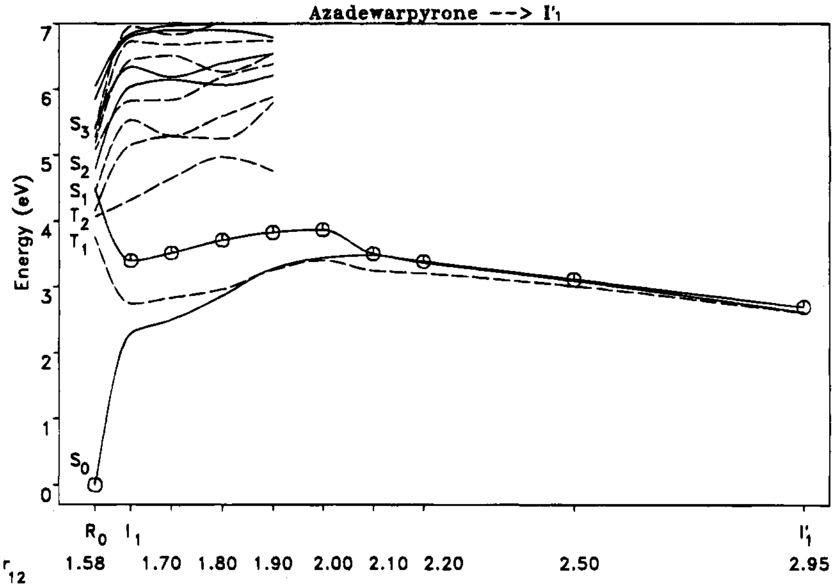

Figure 6. Potential curves for $C^{(1)}$–$C^{(2)}$ bond breaking in the S_1 state; reaction to I'_1, optimized points of geometry (O).

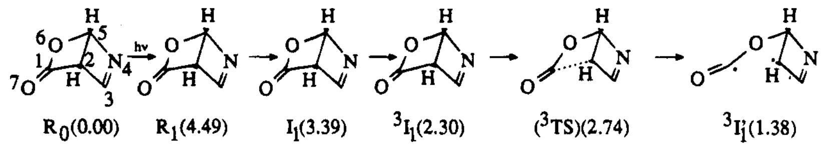

Figure 7. Reaction scheme for $C^{(1)}$–$C^{(2)}$ bond breaking in the T_1 state; reaction to $^3I'_1$.

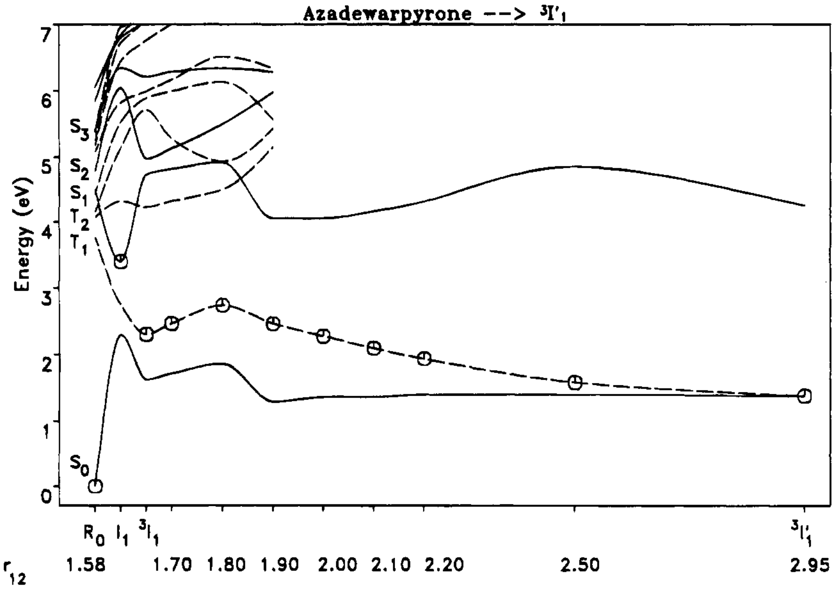

Figure 8. Potential curves for $C^{(1)}$–$C^{(2)}$ bond breaking in the T_1 state; reaction to $^3I'_1$, optimized points of geometry (O).

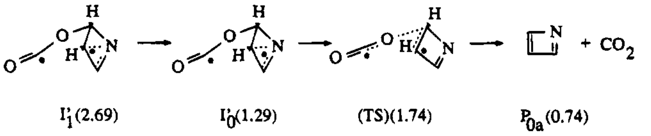

Figure 9. Reaction scheme for formation of azacyclobutadiene.

r_{25} = 2.1 Å IC to the ground state can occur. From this region relaxation to reactant or product is possible. The qualitative course of the potential curve is very similar to the one of the cyclization of α-pyrone.[7] Also in this case the cyclization occurs directly, in agreement with the experiment.[4] Figure 4 shows the reaction scheme of the cyclization in the T_1 state. A reaction in the triplet state can be excluded due to the higher barrier (1.49 eV). In addition, an intersystem crossing (ISC) needs rela-

Table 6. Dihedral Angles φ (deg) of Reactant, Intermediates, and Products of the Photoreaction of Azadewarpyrone

state	ϕ_{1234}	ϕ_{2345}	ϕ_{2156}	ϕ_{5617}	ϕ_{4328}	ϕ_{5439}	ϕ_{34510}
R_0	−72.4	−0.9	−178.3	−176.7	129.5	179.0	−129.4
I_1	−84.0	7.0	−173.8	−172.4	120.5	−131.4	−138.6
I_2	−74.5	−2.0	176.4	166.9	129.2	−177.7	−129.5
$^3I_1$	−80.3	4.5	179.4	179.8	125.1	−122.2	−134.2
I'_1	−72.7	*20.4*	−178.4	112.7	112.4	162.6	−134.7
$^3I'_1$	−68.7	*14.6*	159.4	−157.0	129.1	−174.4	−129.3
I'_0	−72.6	*−16.8*	172.9	176.4	115.4	−173.6	−132.1
P_{0a}		0.0			180.0	180.0	180.0
P_{0b}	−98.6	58.9	150.8	180.0	116.7	171.6	−134.5

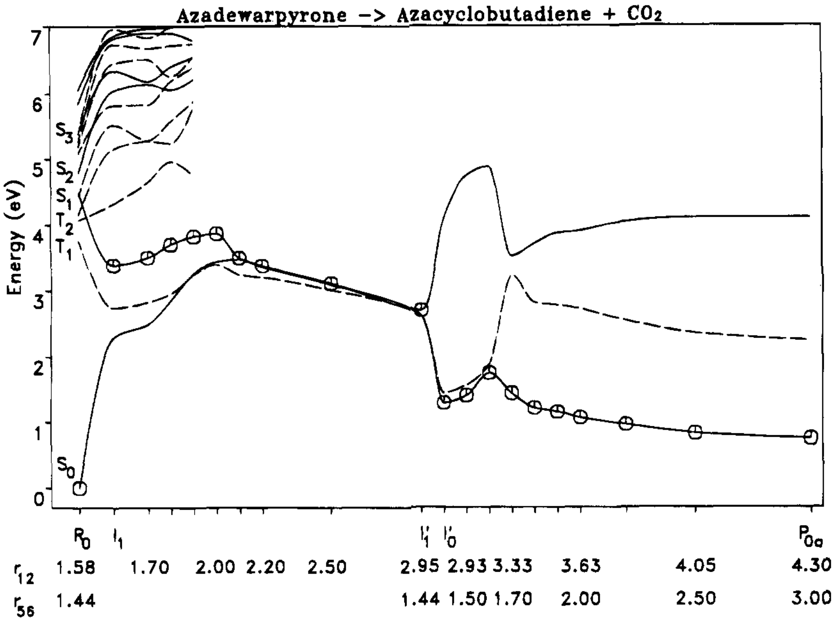

Figure 10. Potential curves for formation of azacyclobutadiene, first step in the S_1 state, optimized points of geometry (O).

Table 7. Valencies of Reactant, Intermediates, and Products of the Photoreaction of Azadewarpyrone

state	V_{12}	V_{13}	V_{16}	V_{17}	V_{23}	V_{24}	V_{25}	V_{34}	V_{45}	V_{56}
R_0	0.893	0.009	0.965	1.889	0.973	0.015	0.957	1.922	0.955	0.944
R_1	0.792	0.012	0.850	1.457	0.950	0.012	0.944	1.882	0.941	0.944
R_2	0.856	0.009	0.947	1.846	0.841	0.053	0.909	1.332	0.724	0.963
I_1	*0.856*	0.013	0.945	1.897	0.951	0.167	*0.754*	1.144	0.845	*0.967*
I_2	0.862	0.019	0.917	1.878	0.900	0.071	0.842	1.279	0.768	1.000
$^3I_1$	*0.875*	0.014	0.944	1.894	0.875	0.018	0.958	1.021	0.954	*0.956*
I'_1	0.012	0.004	0.864	2.017	0.998	*0.349*	0.844	1.435	0.929	0.956
$^3I'_1$	0.004	0.001	0.831	2.028	1.154	0.062	0.958	1.705	0.899	0.947
I'_0	0.034	0.002	0.848	2.032	1.087	0.076	0.946	1.742	0.877	0.958
P_{0a}			1.872	1.872	0.947	0.023	1.919	1.915	0.921	
P_{0b}	0.018	0.916	0.949	1.833	0.962	0.921	0.969	0.917	0.933	0.962

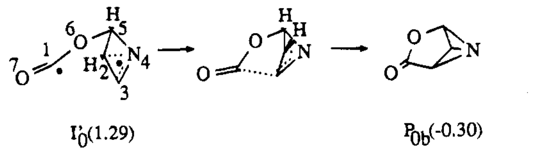

Figure 11. Reaction scheme for formation of azapyrovalene.

tively much time. As a consequence the molecule is found in the lowest vibrational state. From there a further reaction to azadewarpyrone is not possible.

2.2. Photoreaction of Azadewarpyrone. 2.2.1. Stepwise Bond Breaking. The photoreaction of azadewarpyrone starts with an excitation to one of the two lowest excited singlet states, in particular to the S_1 state. Despite the low oscillator strengths of these two states (Table 4) we conclude that excitation to higher states is rather unlikely due to the low excitation energy (4.3 eV) in the experiment. The S_3 state cannot be reached, because it is located more than 1 eV higher than the experimental excitation energy. The low values of the oscillator strengths agree very well with the fact that the photoreaction occurs only by long time irradiation.[4] The geometries of stationary points involved in the reaction on the different potential surfaces are contained in Tables 5 and 6. After excitation into the S_1 state relaxtion to I_1 occurs. For I_1 the bond valence V_{12}[8] of the $C^{(1)}-C^{(2)}$ bond is weaker than in the ground state, whereas the bond valence of V_{56} of the $C^{(5)}-C^{(6)}$ bond is increased (Table 7). This suggests a mechanism where the $C^{(1)}-C^{(2)}$ bond breaks first. The valence of the bridge bond $C^{(2)}-C^{(5)}$ is lowered by 0.2. In the S_1 state the back reaction to 1,3-oxazin-6-one is also possible. Therefore, the cyclization is reversible. After relaxation to I_1, a reaction on the S_1 surface can lead intermediate I'_1 by breaking of the $C^{(1)}-C^{(2)}$ bond. The calculated reaction scheme of this reaction is in Figure 5, the energy profile in Figure 6. If ISC to the T_1 state occurs at I_1, the relaxation to $^3I_1$ takes place. The bond breaking of $C^{(1)}-C^{(2)}$ is possible also on the triplet surface, because the valence V_{12} is reduced also for the intermediate $^3I_1$. Figure 7 shows the reaction scheme and Figure 8 potential curves of the reaction to $^3I'_1$. In both figures r_{12} is the reaction coordinate. This distance was stepwise increased starting from I_1 or $^3I_1$. The other coordinates of the molecule were fully optimized for each chosen value of r_{12}. The intermediates I'_1 and $^3I'_1$ were optimized with respect to all coordinates. On the S_1 surface a barrier of 0.48 eV (Figure 5) is found, compared to a barrier of 0.44 eV (Figure 7) on the triplet surface. Therefore, the primary bond breaking of the $C^{(1)}-C^{(2)}$ bond is possible in both states. The reaction on the S_1 surface is preferred, because ISC to the triplet state needs relatively much time, which leads to a higher reaction rate in the S_1 state. IC and ISC to the ground state are possible at I'_1 and $^3I'_1$, respectively. On the S_0 surface relaxation to I'_0 occurs, which is not a minimum with respect to the bond formation of $C^{(1)}-C^{(3)}$. The potential surface in this region is very flat. Hoffmann et al.[9] call these structures twixtyles, which behave like intermediates although they are not minima. From I'_0

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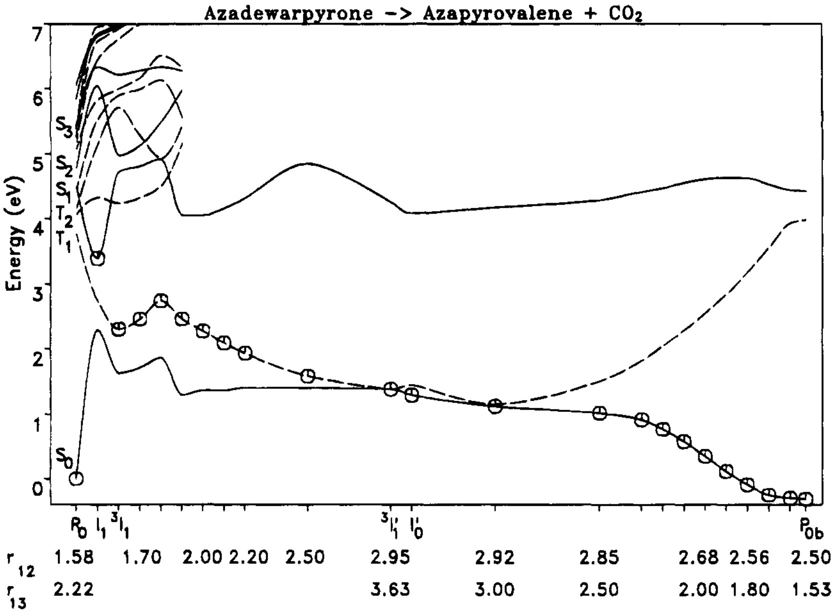

Figure 12. Potential curves for formation of azapyrovalene; first step in the T_1 state, optimized points of geometry (O).

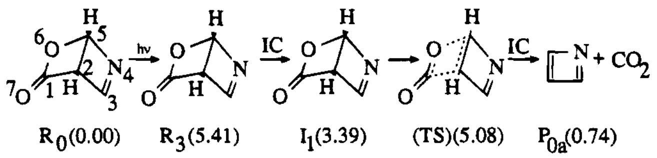

Figure 13. Reaction scheme for simultaneous fragmentation of azadewarpyrone in the S_1 state.

various reactions are possible. Figure 9 shows the reaction scheme and Figure 10 the energy profile of the reaction to azacyclobutadiene. The potential curves in Figure 10 correspond to those in Figure 6 up to intermediate I'_1. At I'_1 the molecule moves to the ground state by IC and relaxes to I'_0. From I'_0 to P_{0a} the distance r_{56}, which was stepwise increased, was the main reaction coordinate. The calculated barrier is 0.45 eV (Figure 9). Therefore, the formation of azacyclobutadiene is possible under the experimental reaction conditions, if the primary bond breaking of the $C^{(1)}-C^{(2)}$ bond occurs on the S_1 surface. After IC from I'_1 to the ground state the molecule possess sufficient vibrational energy to overcome the barrier. For a reaction on the T_1 surface, the molecule would relax in the direction of the product tricyclo[2.1.1.0^{5,6}]-5-aza-3- oxahexan-2-one, in the following called azapyrovalene, after ISC to the ground state. The formation of the tricycle occurs by bond forming of $C^{(1)}-C^{(3)}$ (Figure 11). The energy profile in Figure 12 shows no barrier for this reaction on the ground state surface. Figure 12 is analogous to Figure 8 until $^3I'_1$. At $^3I'_1$ the transition to the ground state occurs by ISC and subsequently relaxation to I'_0. From I'_0 the reaction coordinate is r_{13}. If r_{13} is stepwise decreased starting from I'_0 and the other coordinates are optimized, the potential curves in Figure 12 are obtained. Figure 11 shows the corresponding reaction scheme from I'_0. The formation of azapyrovalene is favored by the relatively short distance r_{24} (Table 5) and the weak bond $C^{(2)}-N^{(4)}$ of I'_1 indicated by the valence V_{24} (Table 7). Under the

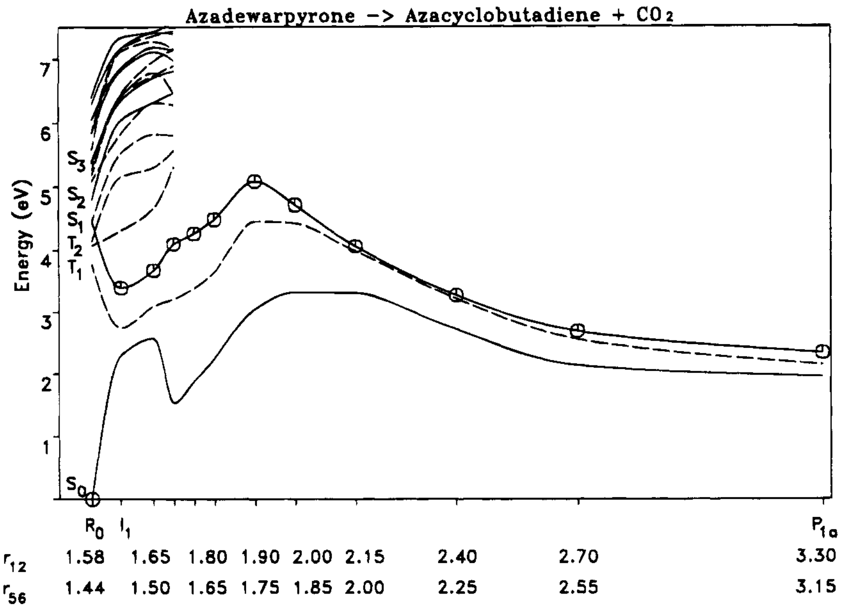

Figure 14. Potential curves for simultaneous photofragmentation of azadewarpyrone in the S_1 state; optimized points of geometry (O).

experimental reaction conditions,[4] this product can lose CO_2 after excitation and can be converted into azacyclobutadiene and CO_2. An analogous structure, tricyclo-[2.1.0^{5,6}]-3-oxahexan-2-one, is assumed by experimentalists in the photochemical methanolysis of α-pyrone[10] and occurs in the thermal rearrangement of bicyclo[2.2.0]-pyran-2-one.[11] Similar to the reaction of α-pyrone[7] we did not find a zwitterionic intermediate as would be suggestive from experimentalists' models for the mechanism of α-pyrone.

2.2.2. Simultaneous Fragmentation. The valence V_{56} of I_1 is increased compared to R_0. Therefore, a simultaneous bond breaking of the $C^{(1)}-C^{(2)}$ and $C^{(5)}-O^{(6)}$ bonds is not to be expected. Figure 14 shows the potential energy curves for simultaneous fragmentation in the S_1 state. The barrier for this mechanism is 1.32 eV (Figure 13). This barrier cannot be overcome in an argon matrix at 8 K. The simultaneous elimination is only possible, if the excitation is at least to the S_3 state. The reaction coordinates in Figure 14 are the distances r_{12} and r_{56}, respectively. The optimized points on the S_1 surface are obtained, if a linear interpolation from I_1 to P_{1a} is performed and the obtained geometries are optimized except for r_{12} and r_{56}. For the structure P_{1a} azacyclobutadiene and CO_2 are optimized at distances $r_{12} = 3.30$ Å and $r_{56} = 3.15$ Å.

3. Conclusion

Our calculations predict that the cyclization of 1,3-oxazin-6-one proceeds via internal cyclization. This is similar to α-pyrone and in agreement with experiment. Azacyclobutadiene is formed from azadewarpyrone as assumed by experimentalists. Under the experimental conditions of long time irradiation there is possibly a secondary photoreaction, whereby the formed azacyclobutadiene is converted into HCN and C_2H_2. The mechanisms of the synthesis of azacyclobutadiene proceeds via a stepwise bond-breaking process, where in the first step the $C^{(1)}-C^{(2)}$ bond is broken in the T_1 or S_1 state. In the second step the breaking of the $C^{(5)}-O^{(6)}$ bond occurs on the ground state surface. Both reaction parts show barriers which can be overcome under experimental conditions. Therefore, a simultaneous elimination of CO_2 does not occur. A photorearrangement of azadewarpyrone to azapyrovalene is possible. Azapyrovalene can be photochemically converted into azacyclobutadiene and CO_2. The photoreaction mechanisms of 1.3-oxazin-6-one and α-pyrone are identical.[7] Both the cyclization and the subsequent fragmentation follow the same mechanism.

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

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