acid 1 and the chiral auxiliary 4. While over reduction with Raney nickel and only marginal selectivity between the two thioxanone C–S bonds with tributyltin hydride were disappointing, an ester saponification/calcium (2 equiv) in liquid ammonia reduction[21] sequence worked nicely regenerating the unchanged chiral auxiliary in 84% yield and liberating the pentenoic acid in 69% yield and 88% ee. Not suprisingly, the saponification step causes some epimerization of the Cα-stereocenter, but this is of no consequence since this stereocenter is removed in the C–S reduction step. The salient features of this four-step, three-pot conversion of α-diazo ester 3 to Cβ-chiral pent-4-enoic acid 1 are nicely illustrated in Scheme III for 9 → 11 (39% overall yield).

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Supplementary Material Available: Spectral data for **2b**, (*Z*)-**3**, **4**, and **5** as well as X-ray crystallograhphic data for *S*-methyl thioxonium salt **2b-X** (13 pages). Ordering information is given on any current masthead page.

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Articles

SINDO1 Study of the Photoisomerization of 2-Cyanopyrrole to 3-Cyanopyrrole

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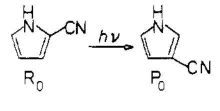
The mechanism of the photochemical isomerization of 2-cyanopyrrole to 3-cyanopyrrole was investigated with the semiempirical MO method SINDO1. Potential energy hypersurfaces of excited states and transition structures of the ground state were calculated with limited configuration interaction (CI) for a qualitative explanation of the reaction pathway. The first reaction step is an internal cyclization which occurs via a minimum on the first excited singlet surface. From there a radiationless transition leads to the ground-state surface. On the ground-state surface either a back reaction to the reactant or a [1,3] sigmatropic shift of the NH group takes place. The latter forms 2-cyano-5-azabicyclo[2.1.0]pentene, which reacts by ring opening to 3-cyanopyrrole. This rearrangement mechanism is unfavorable for furan because the barrier for the 1,3-oxygen migration is much higher than for rearomatization.

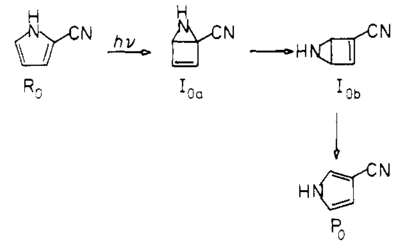
Introduction

In the photoisomerization reaction of many heterocyclic five-membered aromatic rings a permutation of ring atoms takes place. Frequently two neighboring atoms are exchanged. Different product yields and byproducts are obtained dependent on the heteroatom in the ring. As explanation for this fact, different reaction mechanisms were proposed for different heterocycles.[1]

2-Cyanopyrrole reacts under radiation with UV light to 3-cyanopyrrole with a yield of 55%.[2] The reaction is temperature dependent; no isomerization takes place at −68 °C.[2-4]



The following internal cyclization–isomerization mechanism was proposed: As a first step a bond between atoms $C_{(2)}$ and $C_{(5)}$ is formed. The second reaction step is a [1,3] sigmatropic shift of the NH group followed by the ring opening to 3-cyanopyrrole.



Nishimoto et al. have reported in ab initio calculations[5,6] about the internal cyclization mechanisms for oxazole and thiophene. For oxazole a participation of a triplet state in the reaction was found; for thiophene is was found that the [1,3] sigmatropic shift occurs on an excited surface. For pyrrole the experimentalists[2-4] have no indication for the participation of a triplet state and the [1,3] migration of the NH group is considered as a thermal reaction, i.e. on the ground-state surface. Skancke[7a,b] has investigated

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Table I. Vertical Excitation Energies (eV) of 2-Cyanopyrrole

		energy					
state	excitation	*a*	*b*	*c*	*d*	*e*	oscillator strength[a]
$R_1(^1A_2)$	π-σ^*	3.90 (w)			4.38 (w)		10^{-4}
$R_2(^1B_1)$	π-σ^*	4.65 (w)			4.49 (w)		10^{-3}
$R_3(^1B_1)$	π-σ^*	5.60 (vw)					10^{-5}
$R_4(^1B_2)$	π-π^*	6.23 (vs)	5.71 (vs)	5.45 (vs)	5.04 (vs)	4.99 (vs)	0.2
$R_5(^1A_2)$	π-σ^*	6.56 (w)					
$R_6(^1A_1)$	π-π^*	7.02 (s)	6.80 (s)	6.57 (s)	5.53 (s)		10^{-2}
$R_7(^1B_2)$	π-π^*		7.49 (s)	6.73 (s)	5.68 (s)	5.48 (s)	

[a] Calculated with 18 × 18 CI. [b] Calculated with 30 × 30 CI, all π-π^* excitations included. [c] Calculated with 50 × 50 CI as *b* and an equal number of σ-σ^* excitations of symmetry B_2 and A_1. [d] Experimental, this work. [e] Experimental, ref 23.

a thermal [1,3] migration of CH_2 in bicyclo[2.1.0]pentene by ab initio calculations. His first calculated transition structure has C_s symmetry,[7a] whereas the latest calculation[7b] shows C_1 symmetry. We found also only C_1 symmetry for our transition structure. The species with C_s symmetry is a minimum on the hypersurface.

In this work a theoretical study of the photoisomerization of 2-cyanopyrrole was chosen because experiments on this compound were available for comparison. The cyano group should favor the intermediate 2-cyano-5-azabicyclo[2.1.0]pentene (I_{0b}) compared to the intermediate 1-cyano-5-azabicyclo[2.1.0]pentene (I_{0a}), since the double bond of cyclobutene is conjugated with the triple bond of the cyano group for I_{0b}. To estimate the influence of the cyano group we studied the transition structure for the NH migration also in the case of the unsubstituted 5-azabicyclo[2.1.0]pentene. The geometries and corresponding energies of all states involved in the reaction were calculated for all isomers occuring during the reaction. On the basis of this information the reaction process was explained.

For furan derivatives the photoisomerization leads also from 2-substituted to 3-substituted furans. However, furan reacts with low yield and according to a different mechanism which is characterized as ring contraction–ring expansion mechanism.[8-11] In an earlier paper[12] we investigated this mechanism, and it was shown that a cascading sequence of internal conversion and intersystem crossing processes is necessary to explain the reaction mechanism. To understand the different mechanisms for furan and pyrrole, we investigated the internal cyclization–isomerization mechanism of this work also for furan and compared the results. We did not investigate the ring contraction–ring expansion mechanism for pyrrole because it had a low yield for furan due to many branchings on the excited surfaces and back reaction to the reactant. This situation would be expected to be similar in pyrrole.

Method of Calculation

The calculations were performed with the semiempirical MO method SINDO1.[13] This method was already successfully applied for the photoisomerization and photofragmentation of other five- and three-membered rings, e.g. cyclopentanone,[14] substituted diazirines,[15] and 2-methylfuran.[12] We shall use the following notations. The minimum of the ground state of 2-cyanopyrrole will be denoted by R_0. The vertical excitations at this geometry will be denoted by R_1, R_2, R_3, R_4, triplet states by $^3R_1$, etc., intermediates on the ground state surface by I_{0a}, I_{0b}, etc. and transition structures by TS_{0a}, etc. A minimum on the first excited singlet surface is denoted by I_1. Minima are characterized by positive roots of the force constant matrix, whereas transition structures have one negative root.

Geometries of all structures presented in the tables and figures were optimized. Ground-state geometries were located by complete geometry optimization by a Newton–Raphson procedure.[16,17] Bond lengths were optimized within 0.001 Å and bond angles within 0.1°. Transition structures TS and excited state intermediates I_1 and I_2 were optimized on CI surfaces. Further details of the optimization procedure can be found in the furan treatment.[12]

The size of configuration interaction was adjusted according to the need for an unambiguous qualitative explanation of the mechanism. To achieve this we started for the vertical excitation with an 18 × 18 CI which included all single excitations from the two highest occupied to the four lowest unoccupied MO's plus the HOMO–LUMO double excitation. This includes the most important π-π^* excitation which governs the initiation of the reaction. We then emphasized in a larger 30 × 30 and 50 × 50 CI the correlation of those excitations which are involved in the photoprocess. Similar ways for the selection of important configurations in photochemical reactions have been recently suggested by Klessinger[18] and Troe.[19]

Results and Discussion

1. **Experimental Part.** Measurement of the UV spectrum of 2-cyanopyrrole was prepared from pyrrole in two steps via pyrrole-2-carbaldehyde as described in the literature.[20,21] The aldehyde was recrystallized after distillation ($bp_{4\,Torr}$ = 65 °C) with boiling petroleum ether. 2-Cyanopyrrole could not be separated from the unconverted aldehyde by distillation. So we used flash column chromatography with silica gel as the solid phase and a (1:1) mixture of petroleum ether and methyl *tert*-butyl ether as solvent. 2-Cyanopyrrole flowed faster than the aldehyde. From the fractions containing only product the solvent was evaporated, and subsequently the 2-cyanopyrrole was isolated by Kugelrohr distillation. The product was a colorless oil. It was identified as 2-cyanopyrrole by comparison of its NMR spectrum with NMR data from the literature.[22] The NMR spectrum agreed quantitatively

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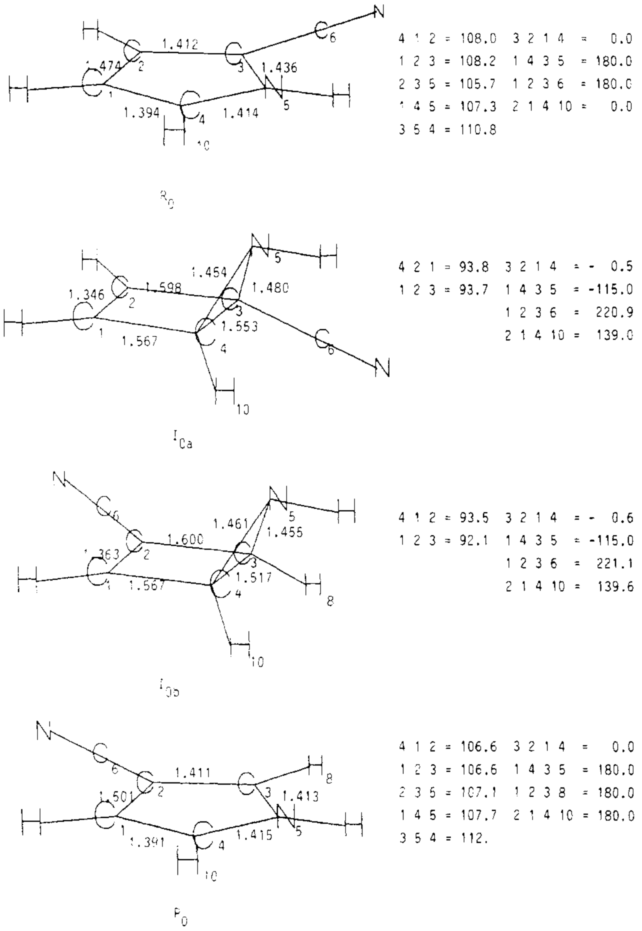

Figure 1. Ground-state geometries of R_0, I_{0a}, I_{0b}, and P_0.

with the literature data. In this paper[22] an elemental analysis was quoted.[23] We measured UV spectrum in methanol with a Beckman spectrometer type 3600 at room temperature. The following bands were found (Table I): A very strong (vs) band at 5.04 eV, two strong (s) bands at 5.53 and 5.68 eV, and two week (w) bands at 4.38 and 4.49 eV. According to the literature two strong bands are located at 4.99 and 5.48 eV with the former being the stronger of the two.

2. Ground-State Geometries. The ground-state geometries of reactant 2-cyanopyrrole (R_0), intermediates 1-cyano-5-azabicyclo[2.1.0]pentene (I_{0a}) and 2-cyano-5-azabicyclo[2.1.0]pentene (I_{0b}) and of product 3-cyanopyrrole (P_0) were located on the SCF hypersurface. They are presented in Figure 1. The numbering of the atoms is for computational convenience. For each intermediate we found two conformers, an endo form with the NH hydrogen tilted toward the four-membered ring, and an exo form with the NH hydrogen tilted away from the four-membered ring. The exo form was thermodynamically more stable in both conformers, and therefore it was used in the following calculations. For the comparison between furan and pyrrole the geometries of the unsubstituted reactants furan $R_0(O)$ and pyrrole $R_0(N)$ were located together with the bicyclic forms 5-oxabicyclo[2.1.0]pentene $I_{0a}(O)$ and 5-azabicyclo[2.1.0]pentene $I_{0a}(N)$.

3. Vertical Excitations of 2-Cyanopyrrole. The comparison of the calculated spectra with experimental data is presented in Table I and Figure 2. The vertical excitations were initially calculated with a 18 × 18 CI with all single excitations from the two highest occupied MO's into the four lowest unoccupied MO's and the HOMO–LUMO double excitation. We found eight triplet states below the ionization limit. Since triplet states play no role for the considered reaction we only list them here. Their irreducible representations are $^3A_2$, $^3B_2$, $^3B_1$, $^3A_1$, $^3B_1$, $^3A_1$, $^3A_2$, and $^3B_2$. The excitation energies are 3.29, 3.53, 3.93, 4.23, 5.14, 5.88, 6.07, and 6.59 eV. We also found six singlet states below the ionization limit for which a comparison with experimental data are given in column a of Table I. To assign calculated excitation energies to experimental UV spectra, the symmetry and oscillator strength of the excited states were considered. In the symmetry consideration we used the C_{2v} symmetry of the ring without substituents.

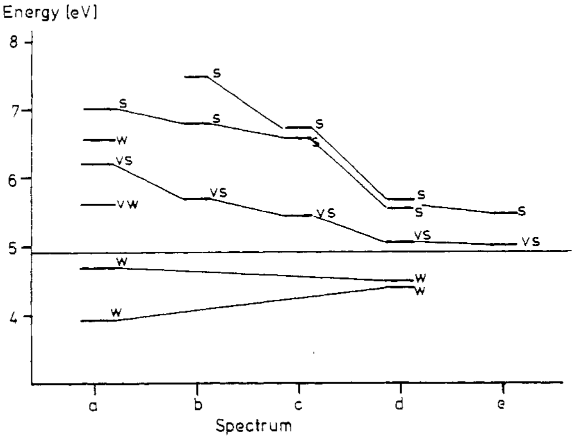

Figure 2. Comparison of calculated and experimental absorption spectra: (a) 18 × 18 CI; (b) all π-π^* excitations; (c) as (b) and σ-σ^* excitations of symmetry B_2 and A_1; (d) experimental; (e) after[23].

At this point agreement of the calculated with our new or the previous experimental data[24] was not too good. We could assign the weak bands at 4.38 and 4.49 eV to R_1 at 3.90 eV and R_2 at 4.65 eV. But the strong experimental bands at 5.04, 5.53, and 5.68 eV had much lower energies than the calculated states R_4 at 6.23 eV and R_6 at 7.02 eV with one state missing. To improve the calculation we enlarged the CI to include all π-π^* excitations. This resulted in a 30 × 30 CI which gave an excitation energy of R_4 at 5.71 eV and of R_6 at 6.80 eV with a third excitation R_7 at 7.49 eV. To lower the calculated excitation energy of these states especially of R_4, we added 10 σ-σ^* single excitations of B_2 and A_1 symmetry. The total CI was 50 × 50. Now R_4 was located at 5.45 eV, R_6 at 6.57 eV, and R_7 at 6.73 eV. We felt that the accuracy of R_4 was now sufficient for proper assignment and study of the photochemical reaction starting from this state.

4. Reaction Process on Excited State Hypersurfaces. In a linear interpolation from reactant R_0 to bicyclic intermediate I_{0a} we saw an indication for a minimum of the first excited singlet state, close to a barrier on the ground-state surface. We therefore optimized the first excited singlet in this region. The geometry of minimum I_1 is presented in Table II. Compared to the geometry of the ground state R_0 the bond lengths $C_{(1)}C_{(2)}$ and $C_{(3)}C_{(4)}$ are shortened and the lengths $C_{(1)}C_{(4)}$ and $C_{(2)}C_{(3)}$ are lengthened. The molecule is nonplanar. The nitrogen atom $N_{(5)}$ is bent out of the ring plane. The geometry of this intermediate I_1 is therefore between reactant R_0 and intermediate I_{0a}.

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Table II. Geometries (Å, deg) of R_0, I_2, I_1, and TS_{0c} with Labeling from Figure 1

	r_{12}	r_{23}	r_{14}	r_{35}	r_{45}	r_{34}
R_0	1.474	1.412	1.394	1.436	1.414	2.345
I_2	1.404	1.472	1.453	1.434	1.394	2.102
I_1	1.371	1.474	1.448	1.449	1.377	2.058
TS_{0c}	1.338	1.561	1.526	1.464	1.352	2.008

	α_{214}	α_{123}	α_{235}	α_{145}	α_{453}	δ_{3214}	δ_{1435}	δ_{1236}	δ_{21410}
R_0	108.0	108.2	105.7	107.3	110.8	180.0	180.0	180.0	180.0
I_2	105.4	101.8	113.8	112.0	96.0	171.4	148.6	142.9	−125.8
I_1	102.8	103.6	113.5	115.4	93.5	168.7	149.3	134.3	−124.1
TS_{0c}	104.5	99.8	113.0	118.6	90.8	167.2	154.2	112.2	−148.3

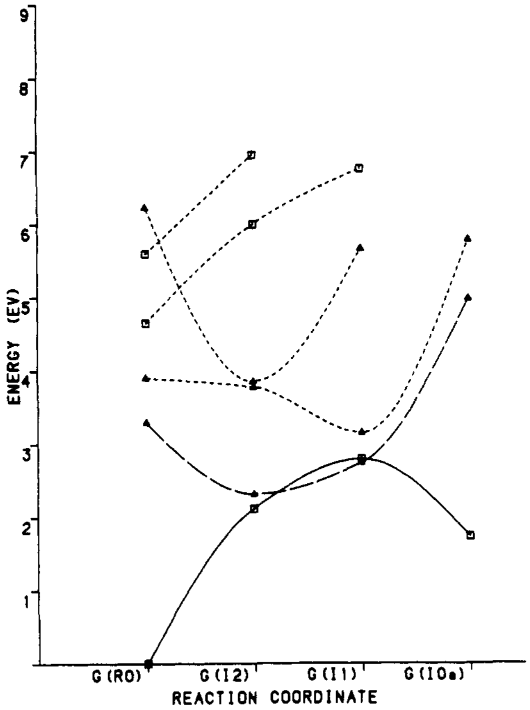

Figure 3. Reaction profile for internal cyclization; (- - -, —) singlet, (– –) triplet.

The reaction profile of the ring-closure reaction is presented in Figure 3. For consistency reasons, we used a 20 × 20 CI for all calculated points. Two double excitations from HOMO to the next two LUMO's were added to achieve quasi degeneracy between S_2 and S_1 at G(I_2). No significant change occurs if the CI is increased to 110 × 110. This CI contained all π-π^* and all important π-σ^*, σ-σ^*, and σ-π^* excitations from the nine highest lying occupied to low lying unoccupied orbitals. To proceed from R_4 to I_1 a crossing of the lower lying states R_1, R_2, and R_3 must take place. If one disregards the substituent, I_1 belongs to point group C_s. If we reduce the symmetry of C_{2v} to C_s under conservation of the plane of reflection σ_v we must correlate A_1 and B_1 with A′ and A_2 and B_2 with A″. In C_s R_1 and R_4 are characterized by A″ and R_2 and R_3 by A′. The crossing of R_4 with R_3 and R_2 is therefore symmetry allowed, but with R_1 symmetry forbidden, resulting in a minimum I_2 in a region of an avoided crossing. Due to the closeness and shape of the two surfaces in the neighborhood of this weakly avoided crossing, the optimization of I_2 could only be achieved within 0.005 Å for bond lengths, 1° for bond angles, and 3° for dihedral angles for several coordinates. From here the system proceeds to I_1. Since the first exicted singlet surface is here only 0.36 eV above the ground-state surface, a radiationless transition to the ground-state surface is feasible.[14]

Figure 4 contains the complete reaction scheme; the left portion contains the reaction scheme for bicyclization.

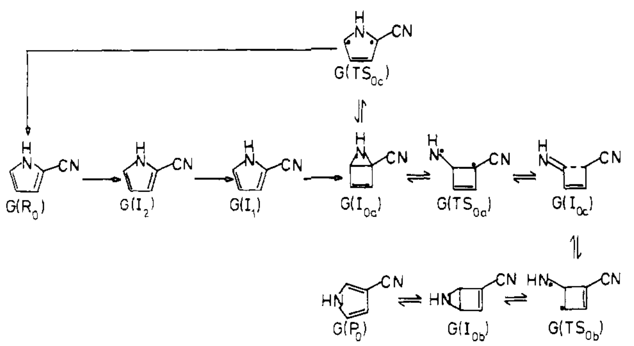

Figure 4. Reaction scheme: G(R) = geometry of minimum or transition structure R.

From the excited reactant the minimum I_2 of the initial surface R_4 is reached first. Here internal conversion takes place to the lowest excited singlet surface which leads to the minimum I_1. There transition to the ground state can occur. On the ground-state surface the system proceeds to the bicyclic intermediate I_{0a}. Its energy is 1.74 eV above that of the reactant R_0. The reaction then proceeds on the ground-state surface as a thermal reaction.

5. Reaction Process on the Ground-State Surface. In the process of reaction from bicyclic form I_{0a} to I_{0b} a [1,3] sigmatropic migration of the NH group must take place. In contrast to a [1,3] hydrogen migration this migration is Woodward–Hoffmann allowed since a p orbital at nitrogen is participating in the reaction which allows a change of sign of the considered MO. Since the HOMO of the π system can change its sign, overlap between the π MO and the p orbital at N is possible, a situation which cannot occur with an s orbital at H.[25]

In the process of NH migration for the unsubstituted 5-azabicyclo[2.1.0]pentene I_{0a}(N) we searched also for a symmetric transition structure. These calculations for intermediates and transition structures were initially done for geometry optimization with a 4 × 4 CI which contains HOMO–LUMO single and double excitations. This is not uncommon in semiempirical methods which are parametrized on SCF ground-state surfaces. We found that the symmetric structure was a local minimum rather than a transition structure. This minimum was in between two unsymmetric transition structures for which the nitrogen atom $N_{(5)}$ extends a bonding interaction with one of the two carbon atoms $C_{(3)}$ or $C_{(1)}$ (Figure 4). We did not find a transition structure for a single-step migration of the NH group over the ring. An analysis showed that steric hindrance prevents this direct migration. For such a pathway the core–core repulsion increases more than the electronic energy decreases.

According to Salem[26] diradicals are characterized by a singlet–triplet degeneracy. For the transition structures

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Table III. Geometries (Å, deg) of TS_{0a}, I_{0c}, TS_{0b} of 2-Cyanopyrrole and of $TS_{0a}(N)$, $I_{0c}(N)$ of Pyrrole with Labeling from Figure 1 (UHF Values in Parentheses)

	r_{12}	r_{23}	r_{14}	r_{34}	r_{45}
TS_{0a}	1.359	1.494	1.546	1.547	1.398
I_{0c}	1.351	1.440	1.567	2.051	1.277
	(1.385)	(1.476)	(1.556)	(1.595)	(1.404)
TS_{0b}	1.415	1.420	1.521	1.567	1.400
$TS_{0a}(N)$	1.372	1.460	1.529	1.519	1.407
$I_{0c}(N)$	1.378	1.378	1.707	1.707	1.280
	(1.416)	(1.416)	(1.560)	(1.560)	(1.407)

	α_{214}	α_{123}	α_{234}	α_{143}	α_{145}	δ_{2314}	δ_{3145}	δ_{1236}	δ_{3219}
TS_{0a}	93.7	93.7	93.3	88.1	112.5	184.4	−104.9	211.6	191.7
I_{0c}	123.6	81.6	93.3	58.7	121.7	165.7	−108.7	250.3	143.2
	(95.9)	(91.8)	(90.7)	(81.4)	(120.8)	(174.6)	(−122.7)	(222.3)	(179.9)
TS_{0b}	92.3	93.4	90.2	83.9	98.7	180.0	−59.6	195.5	209.0
$TS_{0a}(N)$	93.1	92.2	90.2	84.1	109.9	186.3	−103.5	209.6	192.0
$I_{0c}(N)$	108.3	79.0	108.3	61.7	119.2	165.8	−109.5	234.0	126.0
	(93.9)	(91.2)	(93.9)	(80.9)	(115.0)	(177.5)	(−113.4)	(171.5)	(188.5)

Table IV. Energies (eV) of Minima and Transition Structures Involved in the Ground State Reaction of 2-Cyanopyrrole, Pyrrole, and Furan

	$G(R_0)$	$G(TS_{0c})$	$G(I_{0a})$	$G(TS_{0a})$	$G(I_{0c})$	$G(TS_{0b})$	$G(I_{0b})$	$G(P_0)$
R_0	0.00	2.64	1.74	3.33	2.29	3.26	1.58	0.07
$^3R_1$	3.29	2.74	4.99	3.15	5.19	3.40		
$R_0(N)$[a]	0.00	2.64	1.63	3.32	2.96	3.32	1.63	0.00
$R_0(O)$[a]	0.00	3.08	2.53	4.15	3.51	4.15	2.53	0.00

[a] $R_0(N)$ ground state of pyrrole. $R_0(O)$ ground state of furan.

the energy difference between the ground-state singlet and the first triplet is only 0.07 eV. We would therefore classify TS_{0a} and TS_{0b} as diradicals after Salem. The same conclusion is reached with our valence criterion[27] which requires that two atoms of the molecule have a valence number which is reduced by approximately 1 compared to the normal valence number. For TS_{0a} carbon atom $C_{(3)}$ with a valence number of 3.20 and nitrogen atom $N_{(5)}$ with a valence number 2.30 are the radical centers. For TS_{0b} nitrogen atom $N_{(5)}$ has again the valence number 2.30 and $C_{(1)}$ instead of $C_{(3)}$ has the valence number 3.20. So they are the radical centers for TS_{0b}.

The optimized geometries of TS_{0a}, TS_{0b}, and T_{0c} are presented in Table III for the unsubstituted and CN-substituted pyrrole. In the unsubstituted system the intermediate I_{0c} is distinguished from the transition structures essentially by a shortening of the $C_{(4)}N_{(5)}$ bond to 1.28 Å compared to 1.39 Å. The bond order[28] of this bond increased from 1.50 to 1.96. In I_{0c} this bond is close to a double bond. The ring bonds $C_{(4)}C_{(1)}$ and $C_{(4)}C_{(3)}$ are lengthened from 1.53 and 1.52 to 1.70 Å. The lengthening of the $C_{(4)}C_{(3)}$ and $C_{(4)}C_{(1)}$ bonds is a consequence of the shortening of the adjacent $C_{(4)}N_{(5)}$ bond due to the tendency of the migrating N to retain as much bonding as possible. The bond order of these bonds is reduced from 1.08 and 1.11 to 0.90. For this arrangement the carbon atom $C_{(4)}$ is still tetravalent. This atom $C_{(4)}$ tilts out of the ring plane by 14.2° and atom $C_{(1)}$ comes closer to atom $C_{(3)}$ so that a binding interaction with bond order 0.45 arises.

In the case of 2-cyano-5-azabicyclo[2.1.0]pentene I_{0a} the NH migration proceeds as in the unsubstituted case. The difference is that the substituent distorts the minimum I_{0c} considerably. The bond $C_{(4)}C_{(1)}$ increases only by a small amount to 1.567 Å compared to 1.546 Å for transition structure TS_{0a}. The bond $C_{(4)}C_{(3)}$, however, is nearly broken. It elongates to 2.051 Å from 1.546 Å. The average of the $C_{(4)}C_{(3)}$ and $C_{(4)}C_{(1)}$ bonds is close to the unsubstituted case, the asymmetry due to substitution. There is a corresponding reduction of bond order to 0.42 from 1.06. The energy of the substituted I_{0c} is 2.29 eV compared to 2.96 eV for the unsubstituted case.

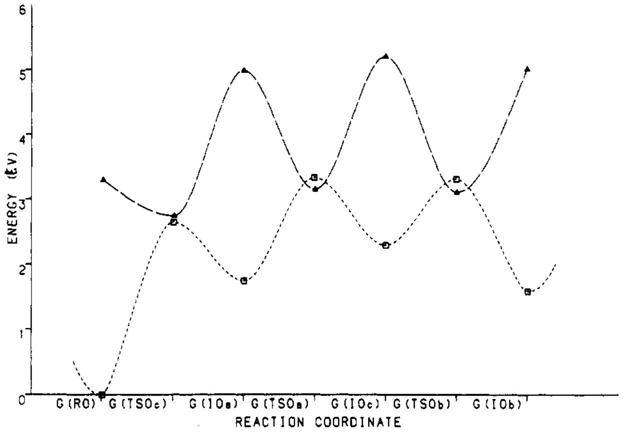

Figure 5. Reaction profile of ground-state reactions; (- - -) singlet, (— —) triplet.

The reaction profile of the NH migration is presented in the right part of Figure 5. From I_{0a} the NH migration takes place via the transition structure TS_{0a} to intermediate I_{0c}, then via transition structure TS_{0b} to intermediate I_{0b}. Energies for these geometries are presented in Table IV. The energies for all states in this table are calculated with the same 4 × 4 CI which is usually sufficient to characterize singlet–triplet degeneracies of diradical states. Whereas the geometry of the minima was determined on the SCF surface, the transition structures had to be optimized on the CI surface. It is important to point out that the intermediate is not a diradical, different from the two transition structures TS_{0a} and TS_{0b}. There is not singlet–triplet degeneracy[26] as can be seen from Figure 5. Also the valence number reduction at two centers[27] is 0.5 for each, not 1 as required for a diradical. We then increased the CI to 19 × 19, which includes single and double excitations from the two highest occupied to the three lowest unoccupied orbitals. In both the 4 × 4 and 19 × 19 CI calculation the SCF configuration accounts for 99% of the

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wavefunction. The barrier for NH migration from I_{0a} to I_{0c} is found as 1.59 eV via TS_{0a}. From I_{0c} the barriers are 1.04 to TS_{0a} and 0.97 to TS_{0b}. It is interesting to note that for the unsubstituted system the barrier from I_0 to TS_{0a} is only 0.36 eV. This is well in line with a barrier 0.26 eV in the latest bicyclopentene study by Skancke.[7b] Via TS_{0b} the system finally reaches bicyclic form I_{0b}. The barrier for back reaction to I_{0a} is with 1.75 eV slightly higher than for the forward reaction since I_{0b} is stabilized by the conjugation of the triple bond of the cyano group with the $C_{(2)}C_{(3)}$ double bond compared to bicyclic form I_{0a}. The equilibrium of the NH migration should therefore be shifted to I_{0b}.

It is now appropriate to point out a discrepancy between the SINDO1 CI calculations of I_{0c} of pyrrole and the ab initio calculations of the corresponding intermediate for bicyclopentene by Skancke et al.[7b] which concerns geometry and character of this structure. Skancke's calculations are based on the unrestricted Hartree–Fock (UHF) method and predict a diradical intermediate. His bond lengths for bicyclopentene are $r_{14} = r_{34} = 1.557$ Å and $r_{45} = 1.495$ Å. From Table III it is apparent that the SINDO1 CI calculation for pyrrole yields quite different values ($r_{14} = r_{34} = 1.707$ Å and $r_{45} = 1.28$ Å). This structure could not be considered as a diradical by standard criteria.[25,26] For cyanopyrrole the ring bonds r_{14} and r_{34} were highly unsymmetric with the ring bond r_{34} adjacent to the cyano group almost broken. To resolve the discrepancy between the SINDO1 CI results and the ab initio UHF results, we have therefore also calculated the structure I_{0c} for unsubstituted and cyanosubstituted bicyclopentene and pyrrole on the UHF level. In addition we have calculated the ground state S_0 and the first excited triplet T_1 of bicyclopentene with the same CI as for pyrrole. The results are the following. On the UHF level the SINDO1 bond lengths for bicyclopentene are very close to those of Skancke et al.[7b] with $r_{14} = r_{34} = 1.56$ Å and $r_{45} = 1.487$ Å. So the discrepancy is not between ab initio and semiempirical data, rather between UHF and CI. Since UHF does not result in a pure singlet, but has triplet admixture, we have also calculated the bicyclopentene triplet T_1 on the CI level. Here the bond lengths are indeed very close to the UHF values with $r_{14} = r_{34} = 1.556$ Å and $r_{45} = 1.460$ Å. Both UHF singlet and CI triplet T_1 are diradicals with atoms 3 and 5 as the diradical centers. The unsymmetry of ring bonds r_{14} and r_{34} is quite small in the cyano-substituted case. The results are very similar for the pyrroles. The geometries of the UHF calculations for pyrroles are listed in Table III in parentheses and confirm the trend in bicyclopentene. These intermediates are also diradicals.

Now we proceed with discussion of the reaction. Another reaction possibility of bicyclic form I_{0a} is the rearomatization to reactant R_0. The ring-opening reaction can proceed for steric reasons only in a disrotatory way. The disrotatory ring opening[29] is accompanied by a HOMO–LUMO avoided crossing which gives rise a to a reaction barrier. To determine the magnitude of this barrier we located the transition structure TS_{0c} leading to reactant R_0. We found a reaction barrier of 0.9 eV. The ring-opening reaction is therefore favored over the NH migration. Only if the vibrational excitation of bicyclic form I_{0a} suffices to surmount the barrier of transition structure TS_{0a}, NH migration takes place. This agrees with the experimental finding that rearrangement of 2-cyanopyrrole to 3-cyanopyrrole takes place under irradiation with UV light at room temperature, but not at −68 °C.

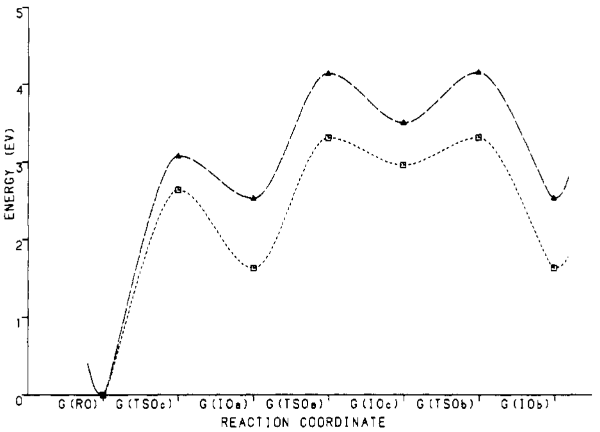

Figure 6. Comparison of reaction profile of ground-state reactions of pyrrole and furan; (- - -) pyrrole, (– –) furan.

The geometry of TS_{0c} is listed in Table II. Compared to intermediate I_{0a} bond $C_{(3)}C_{(4)}$ is broken in TS_{0c}. The distance is 2.00 Å with a bond order of 0.39. The nitrogen atom $N_{(5)}$ is less tilted from the plane for TS_{0c} than for I_{0a}. The energy of the lowest singlet and triplet state is in Table IV. This transition structure is also diradical according to Salem[26] because the singlet–triplet splitting is only 0.1 eV. This agrees with the valence criterion,[27] which determines $C_{(3)}$ and $C_{(4)}$ as the radical centers because of their valence numbers 3.12 and 3.35.

The reason for the high yield of 55% shall be explained as follows. Initially the 2-cyanopyrrole reacts under irradiation to the bicyclic form I_{0a}. This form can aromatize back to reactant R_0 or isomerize to bicyclic form I_{0b}. The latter form can either react back to I_{0a} or proceed to 3-cyanopyrrole. For the final equilibrium the relative energy of I_{0a} compared to that of I_{0b} is important. This is in line with the several hours long duration of irradiation in the experiments.

To make sure that the results reported are qualitatively correct, we have recalculated the extrema on the ground-state surface with a 25 × 25 CI, which consists of the already mentioned 18 × 18 CI plus 7 further double excitations corresponding to the single excitations, and found no significant changes in the relative energies.

6. Comparison of Reaction Mechanisms of Furan and Pyrrole. The comparison of the reaction mechanisms of furan and pyrrole was performed for the unsubstituted systems. Strausz[30] has shown that 5-oxabicyclo[2.1.0]pentene originates from furan under radiation. This is the analogue $I_{0a}(O)$ to $I_{0a}(N)$ for the pyrrole isomerization. The minima and transition structures which play a role in the pyrrole isomerization were investigated for the corresponding oxygen compound. The energies of these systems are contained in Table IV, the reaction profile for the ground states of furan and pyrrole in Figure 6. The starting point for consideration of the continuation of the reaction process is intermediate I_{0a} which is reached via the process depicted in Figure 3. The relative barriers for rearomatization to R_0 and isomerization via I_{0c} to I_{0b} from the intermediate I_{0a} are 0.9 versus 1.59 eV, for $I_{0a}(N)$ versus 1.69 eV, and for $I_{0a}(O)$ 0.55 versus 1.62 eV. The difference between these barriers is substantially higher for the oxygen compound and favors rearomatization much more than for the nitrogen compounds. For furan the rearomatization is much more favored compared to the [1,3] migration than for pyrrole. Therefore the internal cycli-

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zation of furan leads always back to the reactant.

In a simplified reaction scheme for the photoisomerization of furan, a portion of the excited furan reacts to the bicyclic form which reacts back to furan. Only that portion which can avoid this back-reaction can reach the three-membered ring and then proceed to the rearranged product. This is formed in agreement with experiments which show that the rate of furan isomerization can be increased if the irradiation can increase the excitation of triplet states.[31]

For pyrrole the ring contraction–ring expansion mechanism was not considered since its yield would be low in comparison to the internal cyclization–isomerization route due to many branchings on the surface which lead to back-reactions to the reactant. This situation was prevalent in furan.

Conclusion

A qualitative explanation of the mechanism of the photoisomerization of 2-cyanopyrrole is given. The initial excitation is a π-π^* excitation to R_4. The bicyclization to 1-cyano-5-azabicyclo[2.1.0]pentene I_{0a} begins on this surface. Symmetry-allowed crossings with the two lower surfaces of R_3 and R_2 finally leads to an avoided crossing with the R_1 surface. In this region internal conversion leads the system to the lowest excited singlet surface with a minimum I_1. From this minimum another internal conversion facilitates the transition to the ground-state surface. On this surface the intermediate I_{0a} is reached from where NH migration takes place via transition structure TS_{0a}, intermediate I_{0c}, transition structure TS_{0b} to intermediate 2-cyano-5-azabicyclo[2.1.0]pentene. In competition with this pathway ring opening via transition structure TS_{0c} back to reactant R_0 can occur. All three transition structures TS_{0a}, TS_{0b} can be classified as diradicals both according to the singlet-triplet degeneracy criterion[25] and valence criterion.[26] In agreement with experiments it could be shown that the ring opening is energetically favored over the NH migration. This migration can occur only at higher temperatures. The high yield was explained by the lower energy of I_{0b} compared to that of I_{0a}. It was also clarified why furan does not react according to the same mechanism, but according to a more complicated mechanism. Bicyclization is possible also for furan. The energy of the transition structure $TS_{0a}(O)$ for the [1,3] migration of oxygen is, however, rather high compared to $TS_{0c}(O)$ so that the ring opening is much more favored than for pyrrole. The reaction is a cycle of internal cyclization and ring opening without the exit of isomerization which exists in the case of pyrrole. The difference in the photochemical reaction behavior of furan and pyrrole can be explained by a different form of the ground state surface.

Finally it should be emphasized from a technical point of view that smaller CI calculations were systematically enlarged to ensure the reliability of the results.

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Registry No. 2-Cyanopyrrole, 4513-94-4; 3-cyanopyrrole, 7126-38-7.

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Regio- and Stereochemistry of Cross Coupling of Organocopper Reagents with Allyl Ethers: Effect of the Leaving Group

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(Allyloxy)- and (allylthio)benzothiazoles derivatives of dihydropyrans **2** and **4** easily react with methyl cuprates to afford the corresponding *C*-methyl compounds. The only product observed, in each case, was the γ-substitution product with syn stereochemistry. The structures of the products were assigned through the analysis of their ^1H and ^{13}C NMR data.

Methods for the formation of C,C bonds have always been of paramount importance in organic chemistry. They are even more appealing when this goal is achieved with regio- and stereochemical control. Displacements reactions with or without concomitant double-bond shift have been repeatedly used in this context. Many workers have used the cross-coupling reaction of allylic derivatives with a variety of organometallic reagents for synthetic purposes.[1] However the regioselectivity of this process is deeply affected by such factors as solvent, substrate, reagents, catalyst, etc., used. In general it can be said that little regioselectivity has been achieved when working under stoichiometric conditions. For compounds such as allylic carboxylates, and using Grignard reagents in the presence of catalytic amounts of cuprous cyanide, a high degree of regiocontrol can be achieved.[2a]

According to Goering et al.[2a,3] the σ-copper(III) complex initially formed (A) can either undergo stereospecific reductive elimination to give anti-γ-alkylation or isomerize to the π-allyl complex (B), in which case stereochemistry is preserved but regiochemistry is lost (Scheme I). These authors propose RCu(Z)MgBr as the active species. They

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