A Theoretical Investigation of the Pyrazole Phototransposition

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The mechanism of the phototransposition of pyrazole to imidazole was investigated using the semiempirical MO method MNDO. Potential energy surfaces were calculated for S_0, S_1, and T_1. The heights of calculated energy barriers and the experimentally observed photoproducts suggest that the disrotatory electrocyclic ring closure forming a 1,5-diazabicyclo[2.1.0]pentene intermediate and the first [1,3]-sigmatropic shift of nitrogen occur while on an excited state surface. This is followed by internal conversion to the ground state forming a 2,5-diazabicyclo[2.1.0]pentene intermediate. At this point, the intermediate either rearomatizes to an imidazole product or undergoes a second [1,3]-shift forming another 2,5-diazabicyclo[2.1.0]pentene intermediate, which rearomatizes to a different imidazole product. MNDO calculations qualitatively support the experimentally observed product ratios of the two imidazoles that are formed for variously substituted pyrazoles.

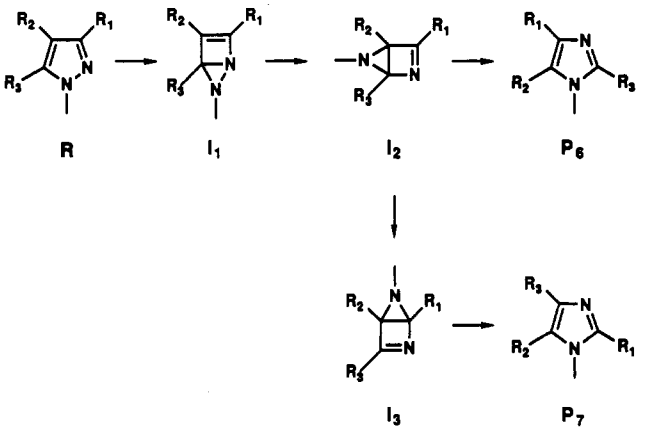
Introduction

The phototransposition chemistry of five-membered heterocycles has been the subject of extensive experimental[1-6] and theoretical studies.[7-12]

Work in this laboratory, for example, has shown that *N*-methylpyrazole undergoes phototransposition by three distinct permutation patterns and, accordingly, by three distinct transposition mechanisms.[13] These permutations can be rationalized by mechanistic pathways initiated by photolytic cleavage of the N-N bond[14] or by initial electrocyclic ring closure followed by one or two [1,3]-sigmatropic shifts of nitrogen. These pathways result in *N*-methylpyrazole → *N*-methylimidazole transpositions with scrambling patterns consistent with the P_4, P_6, and P_7 permutation patterns. Whereas these studies have established the gross structural changes associated with each transposition pathway, we now direct our attention to a detailed electronic description of the structural changes occurring on the ground- and excited-state transposition reaction coordinates.

The phototransposition chemistry of a variety of five-membered heterocycles has been partially or wholly rationalized by the electrocyclic ring closure–[1,3]-heteroatom shift mechanism. In the cases of thiophene[10] and oxazole,[7] ab initio calculations led to the conclusion that the [1,3]-shifts of sulfur and oxygen, respectively, occur while the molecule is on an excited energy surface. Conversely, Jug's theoretical investigations of cyanopyrrole[9] and thiophene[12] suggest that the photochemical electrocyclic ring closure is followed by a ground-state [1,3]-sigmatropic shift of nitrogen and sulfur, respectively.

Scheme I



In this study, the phototransposition of *N*-methylpyrazoles via the electrocyclic ring closure–nitrogen walk pathways has been investigated using computational techniques. The results obtained have been compared to the results of our experimental studies in order to better understand how *N*-methylpyrazoles transpose to *N*-methylimidazoles via this mechanistic pathway.

Method of Calculation

All calculations were carried out using the MOPAC[15] program and the MNDO Hamiltonian[16] with standard parameters. The reliability of the MNDO method for geometries and energies of ground-state nitrogen containing compounds has been documented.[17,18] Recent studies have demonstrated that MNDO and MOPAC can produce meaningful information about excited-state potential energy surfaces.[19-21] Geometries for reactants, products, and intermediates were fully optimized using the Davidon-Fletcher-Powell minimization technique and internal coordinates. Transition structures, located with SADDLE calculations,[22] were refined by minimizing the scalar gradient of energy with respect to the geometry and characterized as saddle points by diagonalizing the Hessian (force constant) matrix[23] and establishing

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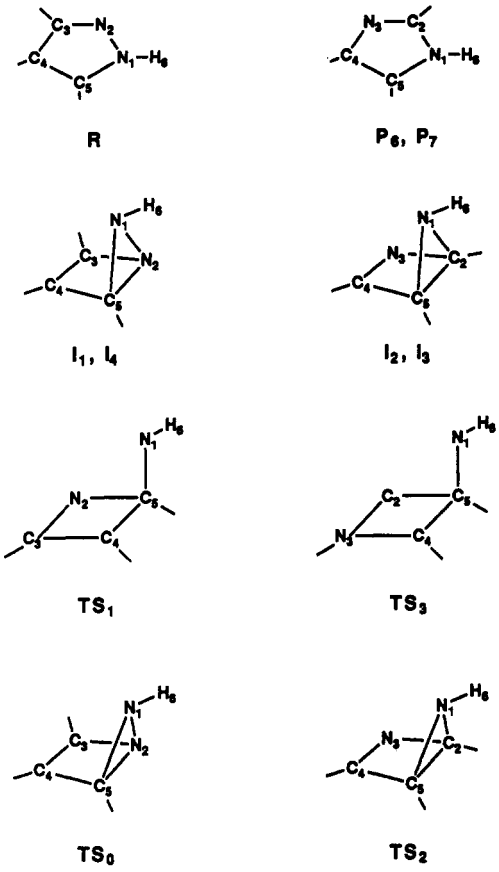

Figure 1. Geometry and numbering scheme of pyrazole, imidazole, intermediates, and transition structures.

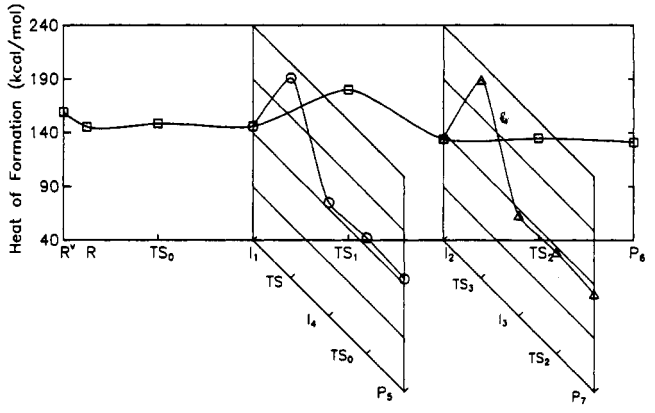

Figure 2. S_1 potential energy surface for the phototransposition of pyrazole to P_5 pyrazole, P_6 imidazole, and P_7 imidazole.

the presence of one and only one negative force constant.

It was not possible to minimize gradients of the transition structures for any of the species studied on the S_1 potential energy surface. As a result, S_1 transition structures were obtained from SADDLE calculations, which provide an approximate transition structure between two intermediates. S_0 and T_1 transition structures were successfully refined with gradient-minimization techniques and were characterized as transition structures with force constant calculations.

In order to simplify the calculations presented here, the unsubstituted pyrazole was used for computing the potential energy surfaces in Figures 2–4, whereas the experimental data are for *N*-methyl-substituted compounds. We have calculated major portions of these potential energy surfaces for *N*-methylpyrazole and find that they differ from the pyrazole results by a nearly constant amount of energy; therefore, conclusions derived from the unsubstituted case should be applicable to the experimental

(23) McIver, J. W.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

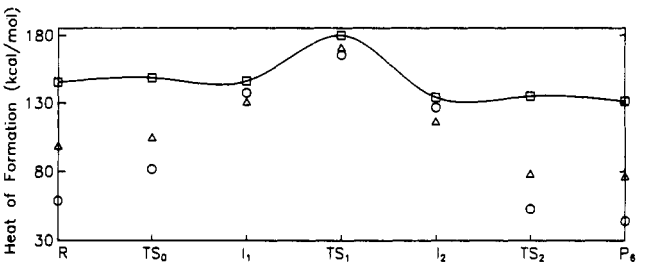

Figure 3. Energies of S_1 optimized geometries indicated with squares. Energies calculated for T_1 and S_0 states using S_1 optimized geometries indicated with triangles and circles, respectively.

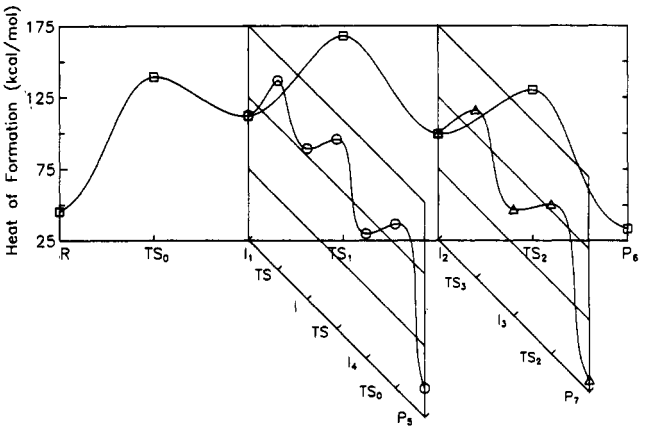

Figure 4. S_0 potential energy surface for the phototransposition of pyrazole to P_5 pyrazole, P_6 imidazole, and P_7 imidazole.

work. Theoretical results that are reported in Table III have been calculated for the complete molecular structure listed.

Calculations of excitation energies and oscillator strengths were also carried out using the HAM/3[24] semiempirical MO method with configuration interaction. The following notations are used. Pyrazole in the ground state is denoted by $R(S_0)$. Vertical excitations of pyrazole are denoted by $R^v(S_1)$, $R^v(S_2)$, etc. Relaxed bicyclic intermediates are denoted as $I_1(x)$, $I_2(x)$, $I_3(x)$, and $I_4(x)$, where x represents the state of the molecule, S_0, S_1, or T_1. Consistent with the permutation pathway by which they are formed, the three possible products investigated in this work are denoted as P_5 (pyrazole), P_6 (imidazole), and P_7 (imidazole).[13] Transition structures are defined by $TS_1(x)$, $TS_2(x)$, etc.

Results and Discussion

1. Optimized Geometries. Pyrazole (R), 1,5-diazabicyclo[2.1.0]pentene (I_1 and I_4), 2,5-diazabicyclo[2.1.0]-pentene (I_2 and I_3), and imidazole (P_6 and P_7) were fully optimized on ground- and excited-state potential energy surfaces. Figure 1 illustrates the geometry and the numbering scheme for the intermediates and transition structures.[25] Pyrazole and imidazole are planar with C_s symmetry in the ground state, however the S_1 and T_1 optimized geometries are nonplanar. Endo and exo conformers of each bicyclic intermediate exist, and these calculations reveal that the exo form is thermodynamically more stable for $I_1(S_0, S_1, \text{and } T_1)$ by 3 kcal/mol, whereas the endo form is thermodynamically slightly more stable for $I_2(S_0, S_1)$.

2. Vertical Excitation of Pyrazole. In the following sections it will be shown that it is not necessary to involve excited states higher than S_1 and T_1 to explain the photochemistry that is observed. The results of HAM/3-CI

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(25) A table showing computed geometric parameters for all structures is available from the authors.

Table I. Vertical Excitation Wavelengths (nm) of Pyrazole

state	excitation	wavelength (nm)	oscillator strength
$R^v(S_1)$	$\pi-\pi^*$	204	0.12
$R^v(S_2)$	$n-\pi^*$	192	0.016
$R^v(S_3)$	$\pi-\pi^*$	187	0.25
$R^v(S_4)$	$\pi-\pi^*$	158	0.78

calculations presented in Table I show that pyrazole can reach S_1 by direct irradiation due to the reasonably large oscillator strength of the $S_1 \leftarrow S_0$ transition.[26] These results differ from those obtained for cyanopyrrole, whose excitation was predicted to be to S_4.[9] The excitation of pyrazole is $\pi-\pi^*$ type with a calculated oscillator strength of 0.12, which is in good agreement with values we calculate from published solution-phase spectra.[27]

The calculated excitation wavelengths are also in good agreement with experiment. $S_1 \leftarrow S_0$ is predicted to occur at λ = 204 nm with HAM/3 and at 251 nm with MNDO. Swaminathan measured the absorption of pyrazole in various solvents and obtained values for λ_{max} between 206 and 210 nm depending on the solvent. The absorption red shifts with increasing solvent polarity, which is consistent with the $\pi-\pi^*$ nature of the transition. Experimentally, the $n-\pi^*$ state has not been observed; however, this is not unreasonable since the weak $n-\pi^*$ absorption may be buried beneath the nearby $\pi-\pi^*$ transition.[28]

3. S_1 Potential Energy Surfaces. The reactants, products, and intermediates were initially optimized on the S_1 potential energy surface. SADDLE calculations were carried out between each set of intermediates along the reaction coordinate in order to determine the height of the energy barriers. Since there are two conformations of the bicyclic intermediates, SADDLE calculations were performed between all combinations of the conformers of I_1 and I_2. In all cases, the transition structures are within a few kcal/mol of each other.

The S_1 potential energy surface for the phototransposition of pyrazole to imidazole via the P_6 and P_7 pathways and for the P_5 pyrazole to pyrazole transposition following the proposed walk mechanism is illustrated in Figure 2. Pyrazole, $R(S_0)$, absorbs a photon and is excited to its S_1 energy state, $R^v(S_1)$. The N_1–N_2 bond length increases from 1.33 to 1.42 Å upon relaxation to $R(S_1)$. This indicates a weakening of the N–N bond in pyrazole. In forming the relaxed excited-state pyrazole, planarity is lost and N_1 moves out of plane by 13°. These calculations thus reveal that the geometry of the S_1 relaxed pyrazole, from which it undergoes disrotatory electrocyclic ring closure, is approaching the geometry of the exo form of the 1,5-diazabicyclo[2.1.0]pentene intermediate $I_1(S_1)$. In the case of $I_1(S_1)$, the nitrogen is approximately 55° above the plane of the molecule. Furthermore, the calculated changes in internuclear distances are consistent with N_2–C_5 bond formation as a result of electrocyclic ring closure. Thus, this distance decreases continuously from 2.28 Å in $R(S_1)$ to 2.10 and 1.88 Å in $TS_0(S_1)$ and $I_1(S_1)$, respectively. While on the S_1 surface, a [1,3]-sigmatropic shift of nitrogen takes place in which the aziridine nitrogen atom walks away from the nitrogen of the four-membered ring. During this nitrogen shift, the N_2–C_5 bond of $I_1(S_1)$ strengthens as the bond distance decreases from 1.88 to 1.51 to 1.43 Å in transforming from $I_1(S_1)$ to $TS_1(S_1)$ to $I_2(S_1)$. This is reasonable since the N_2–C_5 bond of I_1 is no longer part of the highly strained three-membered ring in I_2. Furthermore, during the [1,3]-shift, the N_2–C_3 single bond of I_1 is transformed into a double bond in I_2. This is consistent with the decrease in bond length from 1.41 to 1.32 Å on S_1. Upon formation of the 2,5-diazabicyclo-[2.1.0]pentene intermediate I_2, the molecule could, if it were to remain on S_1, rearomatize forming an imidazole which is consistent with the P_6 permutation pattern, or it could undergo a second [1,3]-shift before rearomatization to an imidazole consistent with the P_7 permutation pattern. Rearomatization of I_2 and I_3 to the P_6 and P_7 imidazoles, respectively, is accompanied by an increase in the C_2–C_5 bond distance from 1.86 to 2.22 Å on S_1. In addition, N_1 returns to the plane of the molecule after being 54° above the plane in I_2 and I_3. It is also conceivable that at I_1, the nitrogen could walk in the opposite direction forming a second 1,5-diazabicyclo[2.1.0]pentene intermediate I_4, which would rearomatize to a pyrazole consistent with the P_5 permutation pattern.

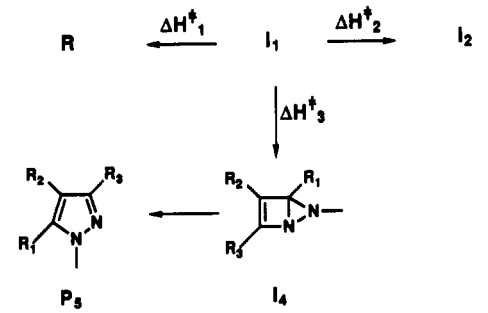

Figure 5. Possible pathways for reaction from I_1.

In order to locate likely cross-over pathways from S_1 to lower energy state surfaces, T_1 and S_0 energies were calculated using the S_1 optimized geometries and are shown in Figure 3. These data show that the potential energy surfaces come very close together at the bicyclic intermediates. The return to the ground state via radiationless transition may occur at $I_1(S_1)$, prior to the [1,3]-shift of nitrogen, or at $I_2(S_1)$, after the walk has occurred. The equilibrium geometries of the bicyclic intermediates on S_1 correspond very closely to the transition structures for rearomatization on S_0. In comparing $I_1(S_1)$ and $TS_0(S_0)$, the corresponding interatomic distances are within 0.02 Å, bond angles are within 1.7°, and dihedral angles are within 1.5°. Since the relaxed potential energy surfaces are calculated to be less than 8 kcal/mol apart at these points, radiationless transfer from S_1 to S_0 is expected to be quite fast due to favorable Franck–Condon factors.

4. Pyrazole–Imidazole (P_6) Phototransposition Path. The S_1 and S_0 potential energy surfaces are shown in Figures 2 and 4, respectively, where all points correspond to optimized geometries. Upon absorption of a photon of light, pyrazole is excited vertically to S_1 followed by rapid relaxation to its equilibrium geometry where it undergoes electrocyclic ring closure to form the 1,5-diazabicyclo-[2.1.0]pentene intermediate $I_1(S_1)$. Upon formation of $I_1(S_1)$, various possibilities for reaction exist. First, since the S_1 and S_0 potential energy surfaces are very close at $I_1(S_1)$ (Figure 3), this geometry should represent a likely cross-over point for an $I_1(S_1)$ to $I_1(S_0)$ radiationless transition to occur.

Upon formation of $I_1(x)$, where x can be S_1, T_1, or S_0, three possibilities for reaction exist. The three pathways are illustrated in Figure 5 and are described as follows. First, I_1 may rearomatize and return to the reactant (R). Second, the aziridine nitrogen may walk away from nitrogen in the four-membered ring and form the I_2 inter-

(26) INDO/S-CI calculations also assign $\pi-\pi^*$ absorption to S_1 with an oscillator strength of 0.102. However, INDO/S inverts the order of S_2 and S_3 from those reported by HAM/3-CI with S_2 (π,π^*) and S_3 (n,π^*).
(27) Swaminathan, M.; Dogra, S. K. *Ind. J. Chem.* **1983**, *22A*, 853–857.
(28) Mason, S. F. *Physical Methods in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1963; Vol. 2, p 60.

Table II. Activation Enthalpies (kcal/mol) for Reaction from $I_1(x)$ and $I_2(x)$

reaction	x = S_0	x = S_1	x = T_1
$I_1(x)$–R(x)	29	3	3
$I_1(x)$–$I_2(x)$	56	31	17
$I_1(x)$–$I_4(x)$	45	81	51
$I_2(x)$–$I_1(x)$	69	46	
$I_2(x)$–$I_3(x)$	43	90	
$I_2(x)$–$P_6(x)$	30	1	

mediate. The third possibility is that the aziridine nitrogen may walk toward the nitrogen in the four-membered ring and form I_4. Competition among these three processes is governed by the relative heights of the energy barriers involved. Activation enthalpies for each pathway are summarized in Table II for unsubstituted pyrazole. The energy barriers for S_1 and S_0 are shown on the potential energy surfaces in Figures 2 and 4.

The activation enthalpies shown in Table II suggest that, of the ground-state pathways available to $I_1(S_0)$, conversion back to the reactant pyrazole should occur with the fastest rate. Furthermore, since the activation enthalpy $\Delta H^{\ddagger}_3$ is 11 kcal/mol lower than $\Delta H^{\ddagger}_2$, on the ground state, the rate of P_5 pyrazole formation should be substantially faster than the rate of imidazole formation via the P_6 pathway. This conclusion is not consistent with the experimental observations, which clearly confirm the absence of pyrazole → pyrazole transposition. Accordingly, it is reasonable to conclude that the first [1,3]-sigmatropic shift is not a ground-state process and that radiationless crossing at $I_1(S_1)$ to $I_1(S_0)$ would be an energy-wasting process leading only to the reactant pyrazole, $R(S_0)$.[29]

Further examination of Table II, however, reveals that on either the S_1 or T_1 reaction coordinate, the energy barrier for formation of I_2, which upon rearomatization forms the P_6 imidazole, is calculated to be substantially lower than for formation of I_4, which upon rearomatization forms the P_5 pyrazole. On the S_1 surface, for example, $\Delta H^{\ddagger}_2$ is predicted to be 50 kcal/mol less than $\Delta H^{\ddagger}_3$, indicating that the rate of the P_5 pyrazole → pyrazole transposition would not be competitive with the rate of the P_6 pyrazole → imidazole pathway. Since this is consistent with our experimental observation, we conclude that the first nitrogen walk is an excited-state process, occurring presumably from the S_1 state,[30] leading to the formation of $I_2(S_1)$.

The S_1 activation enthalpies shown in Table II indicate very high energy barriers for either the reverse $I_2(S_1)$ → $I_1(S_1)$ or the forward $I_2(S_1)$ → $I_3(S_1)$ sigmatropic shifts. Conversely, as expected from symmetry considerations, Table II shows that electrocyclic ring opening of $I_2(S_1)$ to yield the excited singlet state of the P_6 imidazole is a very facile process. It is of interest to note, whereas Figure 3 shows that the S_1–S_0 energy gap is small at I_2, thus predicting that the internal conversion from $I_2(S_1)$ to the S_0 surface is likely, the S_1–S_0 energy gap at the P_6 imidazole is large consistent with inefficient radiationless decay of S_1 imidazole to the ground-state product. It seems likely that the molecule undergoes rapid ring opening–ring closing until it undergoes radiationless transition from $I_2(S_1)$ to $I_2(S_0)$.

As shown in Figure 4 and Table II, $I_2(S_0)$ may either rearomatize to the P_6 imidazole with an activation enthalpy

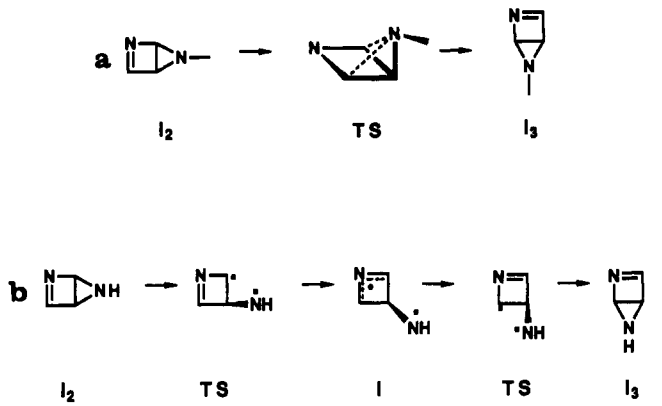

Figure 6. (a) Concerted scheme for nitrogen walk from I_2 to I_3. (b) Biradial scheme for nitrogen walk from I_2 to I_3.

of 30 kcal/mol or it may undergo a nitrogen walk and form a second 2,5-diazabicyclo[2.1.0]pentene intermediate $I_3(S_0)$ with an activation enthalpy of 43 kcal/mol before rearomatization to the P_7 imidazole. It is unlikely that I_1 can be formed from I_2 via [1,3]-sigmatropic shift of nitrogen while on the S_0 surface, since the activation enthalpy is 26 kcal/mol larger than that for formation of I_3 via walk of nitrogen on S_0. Furthermore, $I_1(S_0)$ is thermodynamically less stable than $I_2(S_0)$ by approximately 10 kcal/mol.

5. Concerted vs Biradical Mechanisms. The possibility of biradical involvement in the rearomatization of $I_2(S_0)$ to the P_6 imidazole and in the walk of $I_2(S_0)$ to $I_3(S_0)$ was investigated. Closed-shell potential energy surfaces, as presented in Figure 4, were calculated for both mechanisms. The potential energy surfaces for rearomatization and [1,3]-shift were then recalculated with inclusion of limited configuration interaction (CI). Upon inclusion of CI, the energies of all intermediates in the reaction mechanism changed by less than 4 kcal/mol while the geometry remained virtually the same. Therefore, these structures are nonbiradicaloid, and the energy is taken to be that calculated without CI.

The rearomatization of $I_2(S_0)$ to the P_6 imidazole proceeds via disrotatory electrocyclic ring opening[31] due to steric reasons and is considered to be a forbidden (in the Woodward–Hoffmann sense) concerted process. The transition structure for rearomatization to the P_6 imidazole $TS_2(S_0)$ could only be optimized as a closed-shell molecule and could not be located using CI, suggesting that a biradical structure may not exist between the two closed-shell intermediates. Biradical calculation stabilized the energy of the closed-shell geometry of transition structure $TS_2(S_0)$ by 17.5 kcal/mol; however, geometry optimization with CI of the closed-shell transition structure caused rearrangement to the P_6 imidazole product. It has been argued that biradical energies are calculated to be too low by about 15 kcal/mol because electron correlation has already been accounted for in the parameterization of MNDO and is overcompensated for when CI is included in the calculation.[32] Therefore, we conclude that there is not sufficient stabilization in the energies of the molecules using CI to suggest biradical involvement in the reaction mechanism.

Results of the investigation of the [1,3]-sigmatropic shift of nitrogen from $I_2(S_0)$ to $I_3(S_0)$ are not as conclusive as in the rearomatization case. Potential energy surfaces were

(29) Preliminary calculations suggest that substituents can alter the S_1–S_0 energy gap at I_1 and hence the rate of radiationless crossing before the 1,3-sigmatropic shift occurs. Further studies are in progress.

(30) Attempts to sensitize or quench the transposition with triplet sensitizers or quenchers have been unsuccessful.

(31) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1971.

(32) Dewar, M. J. S.; Fox, M. A.; Campbell, K. A.; Chen, C. C.; Friedheim, J. E.; Holloway, M. K.; Kim, S. C.; Liescheski, P. B.; Pakiari, A. M.; Tien, T. P.; Zoebisch, E. G. *J. Comput. Chem.* **1984**, *5*, 480.

Table III. Summary of P_6 vs P_7 Data

reactant	$\Delta H^{\ddagger}_A$ (kcal/mol)	$\Delta H^{\ddagger}_B$ (kcal/mol)	$\Delta(\Delta H^{\ddagger})$ (kcal/mol)	ΔH_r (kcal/mol)	observed ($P_4/P_6/P_7$)
3-cyano-1,5-dimethylpyrazole[a]	29.7	31.8	2.1	-1.53	4.6/1.6/1
1,5-dimethylpyrazole	29.8	36.7	6.9	-3.30	3.5/1.8/1
N-methylpyrazole	30.6	39.5	8.9	0	4.9/7.2/1
3-cyano-1-methylpyrazole[a]	31.8	35.6	3.8	1.71	2.3/1/-
1,3-dimethylpyrazole	33.2	40.0	6.8	3.30	1.6/1/-
1,4-dimethylpyrazole	29.0	39.2	10.2	0	only P_4
pyrazole	30.1	43.6	13.5	0	

[a] Reference 1.

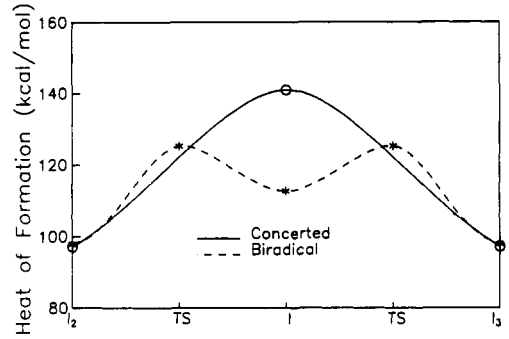

Figure 7. Concerted and biradical potential energy surfaces for the nitrogen walk from $I_2(S_0)$ to $I_3(S_0)$.

calculated for closed-shell and biradical mechanisms. The two mechanisms are illustrated in Figure 6a,b, and the corresponding potential energy surfaces are compared in Figure 7. In considering all of the combinations of the two conformers of the bicyclic intermediates I_2 and I_3, the lowest energy barrier for walking following a concerted process is 44 kcal/mol, whereas the barrier for a biradical mechanism is 28 kcal/mol. In the concerted pathway the transition structure $TS_3(S_0)$ possesses a plane of symmetry perpendicular to the plane of the four-membered ring. The C_4–C_5 and C_2–C_5 bond lengths are equal (1.53 Å), as are the C_2–N_3 and C_4–N_3 bond lengths (1.38 Å). Also, the migrating nitrogen, N_1, is situated directly above C_5 as shown by the N_3–C_2–C_5–N_1 dihedral angle of 87°. However, in the biradical mechanism the molecule passes through a nonsymmetric transition structure before reaching a symmetric intermediate. It should be noted that the biradical potential energy surface is similar to that obtained by Jug[9] in the analysis of the photochemistry of pyrrole, a similar five-membered heterocycle. Since energies obtained with CI are expected to be too low by approximately 15 kcal/mol as previously discussed, these predicted barriers of biradical and concerted mechanisms may not be very different. At the MNDO level, it is difficult to distinguish between the two pathways. The mechanism may be biradical, but the true energy barrier probably lies between the values calculated for the closed-shell and biradical cases.

6. Comparison of MNDO with Experiment. Calculations suggest that the second [1,3]-sigmatropic shift is a ground-state process. In order to test this possibility, ground-state potential energy surfaces have been calculated for several molecules for which experimental data exists. Qualitative support for the observed P_6 imidazole to P_7 imidazole relative product distributions has been obtained from the calculations by a combination of thermodynamic and kinetic considerations. Table III is a summary of the experimental data and the calculated results for several molecules following the scheme shown in Figure 8. P_4 corresponds to the phototransposition product that is obtained via the proposed ring contraction–ring expansion mechanism.[13,33]

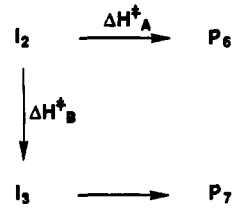

Figure 8. Scheme for analysis of Table III.

In Table III, $\Delta H^{\ddagger}_A$ is the activation enthalpy for rearomatization of $I_2(S_0)$ to $P_6(S_0)$ and $\Delta H^{\ddagger}_B$ is the activation enthalpy for undergoing the [1,3]-sigmatropic shift to form $I_3(S_0)$ from $I_2(S_0)$. $\Delta(\Delta H^{\ddagger})$ is the difference between these two values and ΔH_r is the reaction enthalpy for $I_2(S_0) \rightarrow I_3(S_0)$. A dash indicates that no observable product was obtained.

Qualitatively, as the difference between $\Delta H^{\ddagger}_A$ and $\Delta H^{\ddagger}_B$ increases, the P_6/P_7 product ratio increases. This can be seen for the first three molecules in Table III where $\Delta(\Delta H^{\ddagger})$ increases from 2.1 to 8.9 kcal/mol and the observed product ratio increases from 1.6/1 to 7.2/1. In addition, as ΔH_r changes from exothermic to zero to endothermic, the P_6 to P_7 ratio increases. The first five molecules in Table III illustrate this trend with the amount of P_6 to P_7 products increasing to the point where no P_7 imidazole is observed. A point worth noting from these data is that in cases where it seems reasonable kinetically to form the P_7 imidazole, but unreasonable by thermodynamic considerations (3-cyano-1-methylpyrazole and 1,3-dimethylpyrazole), the P_7 product has not been observed. In the case of 1,4-dimethylpyrazole, only the P_4 imidazole product has been obtained experimentally. However, irradiation of 1,5-dimethylimidazole, the P_6 product of 1,4-dimethylpyrazole, with appropriate deuterium labeling, results in an equilibrium amount of P_6 and P_7 imidazoles. Although the P_6 to P_7 product ratio is not known, the observance of both products is consistent with the kinetic and thermodynamic data of 1,4-dimethylpyrazole in Table III.

Since the [1,3]-shift of nitrogen from I_2 to I_3 and the rearomatization of I_2 to P_6 are predicted to be ground-state thermal processes and the calculated barrier for rearomatization is smaller than the barrier for the [1,3]-shift, the P_6 to P_7 product ratio should be sensitive to temp. changes. Consistent with this theoretical prediction, we have obsd. that photoreaction of 1,5-dimethylpyrazole at 30, 10, 0, -10, and -30 °C results in an increasing P_6 to P_7 product ratio but that the total amount of P_6 and P_7 products formed over this temperature range remains essentially constant.[34]

Our finding that the barrier for rearomatization is smaller than the barrier for walking in the ground state

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is in accord with Barltrop's experimental and Jug's SINDO1 conclusions concerning cyanopyrrole. Photolysis of 1,5-dimethylpyrazole was also carried out at 77 K in frozen acetonitrile resulting in the formation of imidazoles that are consistent with only the P_4 and P_6 permutation patterns. No P_7 imidazole was detected even after 33% of the reactant had disappeared. These observations are consistent with our calculated results, which suggest that I_2 forms on a relatively flat potential energy surface, such as S_1, and that subsequent reactions occur on the ground-state surface.

Conclusion

MNDO calculations and experimental product distributions are used to provide a qualitative explanation of the phototransposition of pyrazole to imidazole via [1,3]-sigmatropic shift of nitrogen. Initial electrocyclic ring closure of pyrazole and walk of nitrogen occur on the S_1 potential energy surface. The return to the ground state is via a radiationless transition from $I_2(S_1)$ to $TS_2(S_0)$. The second [1,3]-shift of nitrogen may be a biradical process; however, it is difficult to clearly distinguish between concerted and biradical mechanisms at the MNDO level. Kinetic and thermodynamic arguments are in qualitative agreement with the experimentally observed relative product distributions of the P_6 and P_7 imidazoles and support the assignment of the second walk to a ground-state process. Photolysis at decreasing temperature results in increasing P_6 to P_7 product ratios. This is consistent with a ground-state thermal reaction and a smaller barrier for rearomatization than walking as suggested by the theoretical calculations.

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Registry No. R, 288-13-1; P_6,P_7, 288-32-4; I_1,I_4, 74613-28-8; I_2,I_3, 74613-34-6.

Structures and Lifetimes of 1,4-Biradical Intermediates in the Photochemical Cycloaddition Reactions of *N*-Benzoylindole with Alkenes[1]

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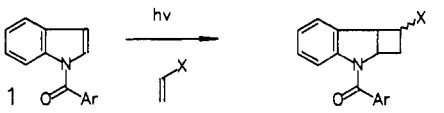
The photochemical cycloaddition reaction of *N*-benzoylindole with 1,6-heptadiene, tetramethylethylene, and vinylcyclopropane has been examined. The structures of the products suggest that the reaction proceeds via a 1,4-biradical intermediate that is formed by bonding between one terminus of the alkene and the 2-position of the indole derivative. This result is used to explain the origin of the previously observed regioselectivity of the photochemical cycloaddition reaction. The biradical intermediates obtained in the photochemical cycloaddition reaction of *N*-benzoylindole with vinylcyclopropane and 1,6-heptadiene can undergo rearrangement reactions whose rate constants can be estimated. Using these rates as clocks, the lifetimes of the intermediate biradicals in the photochemical cycloaddition reaction of *N*-benzoylindole with alkenes are estimated to be of the order of 100 ns. The consequences of this for the potential success of synthetically useful trapping of the intermediate biradicals is discussed.

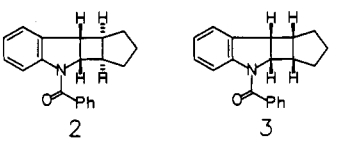
Introduction

It has been reported[2,3] that indoles possessing a benzoyl substituent on the nitrogen atom form cyclobutane products when irradiated with ultraviolet light in the presence of alkenes. With monosubstituted alkenes the reaction is found[3] to be regioselective, but not normally stereoselective, as indicated in Scheme I. This reaction offers a potential route for the synthesis of substituted indoles if methods for elaboration of the cyclobutane ring can be developed. With this as our motivation, we have been examining the mechanism of this photochemical cycloaddition reaction in order that the factors governing the reaction regiochemistry and stereochemistry can be understood. We have previously obtained[4] steady-state kinetic results that suggest that the reaction proceeds as shown in Scheme II. In this scheme, intersystem crossing

Scheme I



of the singlet excited state of *N*-benzoylindole (1) occurs efficiently[5] to yield the triplet excited state, which is intercepted by an alkene such as cyclopentene to give one or more isomeric 1,4-biradical intermediates. The major fates of the biradicals are reversion to the ground-state indole derivative and alkene or closure to the cyclobutane products **2** and **3**. The intermediacy of biradicals that



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partition between product and starting material is sup-

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