Compounds IXa and XIb are obtained in a similar way.

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QUANTUM-CHEMICAL INTERPRETATION OF RECYCLIZATION REACTIONS.

10.* PHOTOISOMERIZATION OF SIX-MEMBERED HETEROCYCLES

Yu. B. Vysotskii and L. N. Sivyakova

UDC 541.141:539.196:547.72'77'78

Singlet photoisomerizations of a number of six-membered heterocycles have been described on the basis of the index approach in the framework of the coupled variant of perturbation theory for a one-electron transition density matrix in the Pariser—Parr—Pople method.

In the preceding investigations of this series we developed a quantum-chemical approach to the description of the recyclization reactions of molecules with conjugate bonds on the basis of the coupled variant of perturbation theory. In the case of dark reactions, the orders of the bonds between not directly bonded atoms of the molecule P_{ik} serve as the reactivity indices. In the case of photochemical reactions of the X type in Dougherty's terminology [2], we obtained [3] more complicated expressions for the reactivity indices $K_{ik}^{S,T}$, to which the main contribution is made by the changes in the long-range bond orders upon excitation of the molecule. This approach was tested in the example of the photochemical contraction reaction of the furan ring [3] and a number of photoisomerizations of five-membered heterocycles [1]. In the present work it was extended to the case of singlet photoisomerizations of six-membered heterocycles.

1. As follows from Table 1, which presents the reactivity indices of singlet photoisomerization of zzines, the excitation of the pyridine molecule (I) results in a sharp increase in the role of the nonclassical structures, particularly of Dewar azabenzene and azaprismane. This is manifested by the presence of large positive values for $K_{2,5}^S$ and $K_{1,4}^S$. At the same time, the sum of these parameters in the first singlet state with the corresponding P_{ik} is close to zero. This is primarily an indication of the possible strong influence of the substituents and even of the solvent on the nature of the transition state, and, in the final

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*For Communication 9, see [1].

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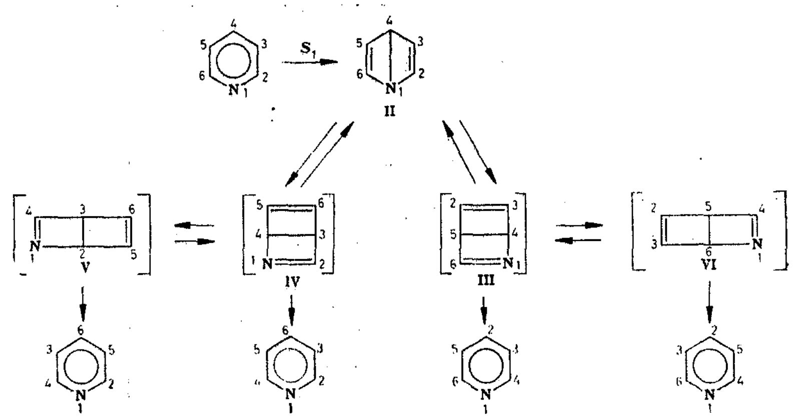
TABLE 1. Reactivity Indices of Singlet Photoisomerizations of Azines K_{ik}^S

Compound	i—k	$P_{ik}(S_0)$	$K_{ik}^s(S_1)$	$K_{ik}^s(S_2)$
Pyridine	1—3	−0,017	−0,022	0,028
	1—4	−0,314	0,322	0,214
	2—4	0,051	−0,076	−0.041
	2—5	−0,338	0,335	0,355
	2—6	−0,066	0,113	0,050
	3—5	−0,005	0,081	−0,039
Pyridinium cation	1—3	−0,077	−0,033	0,093
	1—4	−0,252	0,238	0,251
	2—4	0,206	−0,254	−0,224
	2—5	−0,292	0,322	0,117
	2—6	−0,279	0,408	0,221
	3—5	0,055	0,187	−0,180
Pyridazine	1—3	−0,082	0,088	0,051
	1—4	−0,311	0,319	0,183
	1—5	0,035	−0,082	−0,009
	3—5	0,043	−0,013	−0.038
	3—6	−0,365	0,335	0,575
Pyrimidine	1—3	−0,034	−0,037	0,091
	1—4	−0,317	0,326	0,199
	1—5	−0,022	0,055	−0,043
	2—4	−0,014	0,053	0,048
	2—5	−0,341	0,331	0,519
	4—6	0,104	−0,183	−0,110
Pyrazine	1—3	0,033	−0,096	0,001
	1—4	−0,297	0,307	0,070
	2—5	−0,352	0,360	0,454
	2—6	−0,074	0,206	0.004

analysis, it points out the direction of the photoisomerization. In fact, from [4-7] it follows that the photoisomerization of mono- and dimethylated pyridines in the first singlet state cannot pass through an intermediate of the azaprismane type with an identical relative arrangement of the atoms. Thus, while in the 2,3-dimethylpyridine molecule an intermediate azaprismane might be formed by the bonding of atoms 2 and 6, 1 and 4, and 3 and 5, in the 2,6-dimethylpyridine molecule the isomerization products correspond to the possible formation of a prismane with bonding between atoms 1 and 3, 2 and 5, and 4 and 6 [4, 7, 8].

The description of the photoisomerization products of other isomers of dimethylpyridine requires the introduction of other intermediate states.

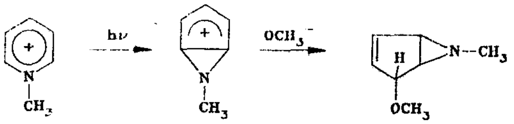
SCHEME 1



Nevertheless, the entire body of existing experimental findings (including those presented above) can be described with the aid of a bicyclic transition state based on Dewar azabenzene II (see Scheme 1). After the cleavage of the 1–2 or 1–6 bond, structure II isomerizes to bicycles III and IV, which, in turn, can be transformed into V or VI and then into the photoisomerization products. According to the experiments in [5-7], it follows from Scheme 1 that 2-methylpyridine and 4-methylpyridine, as well as 2,4-dimethylpyridine and 2,6-dimethylpyridine, undergo interconversions. The irradiation of 3,4-dimethylpyridine gives a mixture of the 2,3 and 2,5 isomers, and the irradiation of 2,3-dimethylpyridine and 3,5-dimethylpyridine do not undergo photoisomerization. We also note that compound II was isolated as an intermediate during the irradiation of pentafluoroethylpyridine [9] and that structures of types III-VI are assumed to be transitional structures in the case of the photohydrogenation of pyridine [4, 10].

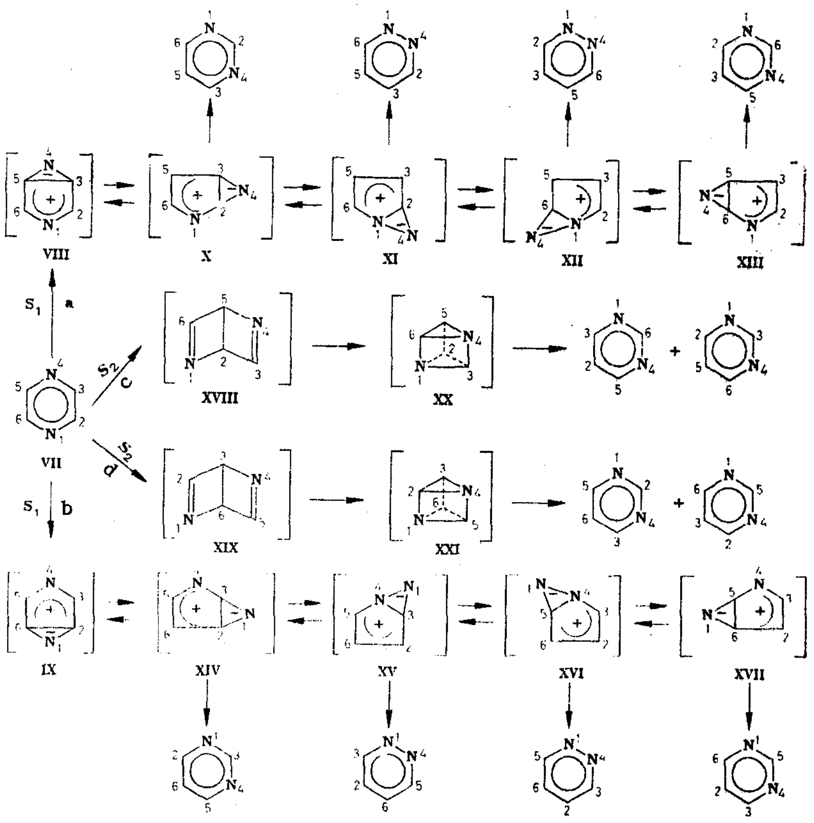
We stress that Scheme 1 is based on the assumption that the initial cyclization of pyridine occurs at positions 1 and 4. This assumption corresponds to the large positive value of $K_{1,4}^S$ (see Table 1), which is apparently enhanced to an even greater degree when methyl groups are introduced into the molecule. As follows from Table 1, the isomerization of pyridine in the S_2 state should involve the intermediate formation of a 2–5 bond.

2. Cyclization at positions 2 and 6 and at positions 3 and 5 is most probable for the pyridinium cation in the first singlet state. This corresponds to the mechanism proposed in [4, 7]

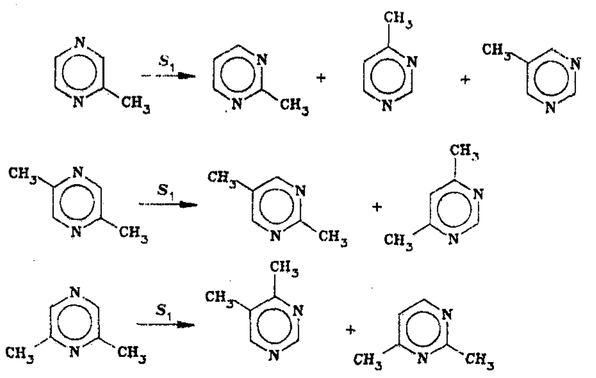


3. As follows from a comparison of the K_{ik}^S for the diazines (see Table 1), in the lowest singlet state the photoisomerization reactions should be most characteristic of the pyrazine molecule (VII).

SCHEME 2



In this case, bonding between atoms 2 and 6 or atoms 3 and 5 (paths a and b in Scheme 2) are most advantageous for the S_1 state. All the numerous experimental data [4, 7, 8, 11, 12] conform to a scheme including the formation of bicyclic intermediates VIII and IX, which are transformed in analogy to the five-membered heterocycles into structures X-XVII and then into the photoisomerization products, viz., pyrimidines and trace amounts of pyridazines. As an illustration we present only a few of the best known examples of such conversions:

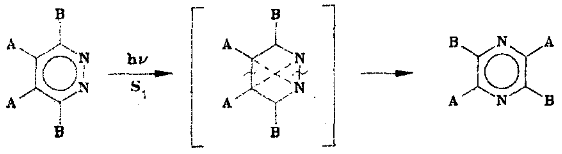


Special mention should be made of the fact that one of the products of the last reaction is 2,6-dimethylpyrimidine (see [8] and the literature cited therein), which conforms to scheme 2, but was not presented in several reviews [12].

In constrast to the S_1 state, in the S_2 state (see Table 1) the pyrazine molecule should be characterized by the appearance of 2—5 or 3—6 bonds (paths c and d in Scheme 2) with the subsequent transformation of Dewar diazabenzenes XVIII and XIX into azaprismanes XX and XXI. The opening of the latter (in analogy to prismane; see, for example, [4]) is followed by the formation of the corresponding pyrimidines. There are still no experimental data on the isomerization of pyrazine in the S_2 state.

4. We shall not dwell on the photoisomerizations in the lowest singlet states of the pyridazine and pyrimidine molecules that are less characteristic than those of pyrazine (compare the values of the K_{ik}^S). We shall only note that the mechanism proposed in [13] (see also [4, 12]) for the photoisomerization of pyridazine (Scheme 3) does not contradict the positiveness of the sum $P_{1.4} + K_{1.4}$ calculated for this molecule (see Table 1). In general, we should again stress the strong dependence of this and other isomerizations with small absolute values of $P_{ik} + K_{ik}^S$ on the nature and positions of the substituents and on the solvent.

SCHEME 3

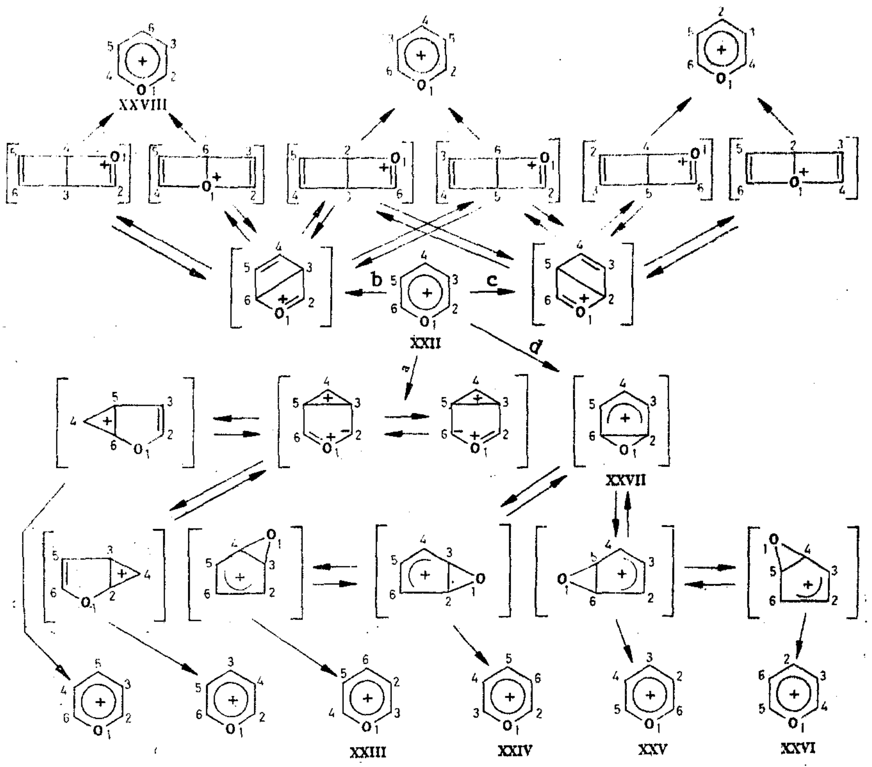


From Table 1 it is seen that the first step in the photoisomerizations in the pyridazine molecule in the S_2 state should be bonding between positions 3 and 6 and that the first step for pyrimidine in the same state should be bonding between positions 2 and 5.

5. In conclusion, we shall mention several photoisomerizations of pyran derivatives. According to the theoretical data ($P_{2.5} = -0.290$, $K_{2.5} = 0.326$, $P_{2.6} = -0.324$, $K_{2.6} = 0.431$, $P_{3.5} = 0.061$, $K_{3.5} = 0.202$). The excitation of pyrylium cation XXII to the S_1 state can result in the rearragments shown in Scheme 4, a particular direction becoming the main direction, depending on the positions of the substituents and their character. For example, path d is predominant in the case of 4-hydroxypyrylium cations, and practically all the presently known photoisomerizations of these cations give isomers XXIII-XXVI (see [4, 14-18]). In

particular, products XXIV and XXV were isolated following the photoisomerization of the 2,6-dimethyl-4-hydroxypyrylium cation [4, 17] (2,4,6-trimethylpyrylium perchlorate undergoes an analogous photoisomerization [14]). With respect to products XXIII and XXVI, they were obtained along with substituted furans as a result of the photoisomerization of the 2,3-dimethyl-4-hydroxypyrylium cation in concentrated sulfuric acid [18]. It has been suggested that intermediate XXVII forms in the first step of this photoisomerization. Information on the photoisomerizations of other derivatives of the 4-hydroxypyrylium cation which also conform to Scheme 5 is given in [7, 16, 19].

SCHEME 4

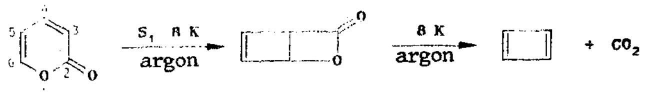


We note that the first step in the well-known photoisomerization of 4-pyrones to 2-pyrones is presumably the formation of the corresponding hydroxy form, which is followed by its recyclization according to Scheme 4 [15, 20-22]. In the case of the 2-hydroxypyrylium cation, path b is predominant (see [15, 17]), and all the isomerization products have structure XXVIII. Path a in Scheme 4 is not realized in any of the known photoisomerizations of the derivatives of the pyrylium cation.

We stress that the "pericyclic" rearrangement of the transition states (see the schemes in the present work and in [1]) has been thoroughly studied and is generally accepted for the interpretation of both thermal and photochemical isomerizations [4, 20, 23].

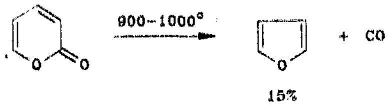
The photoisomerization of 2-pyrone under the action of UV light to a β-lactone condensed with a cyclobutene ring [5, 7, 8, 11, 24-26] is also in good agreement with the data from the calculation in the framework of the approach developed. For example, the maximum value of K_{ik}^S corresponds to positions 3 and 6 and is equal to 0.440, which significantly exceeds the absolute value of $P_{3.6} = -0.311$, and thus correctly describes this isomerization (the values of the sum $P_{ik} + K_{ik}^S$ for the other positions are small or negative).

SCHEME 5



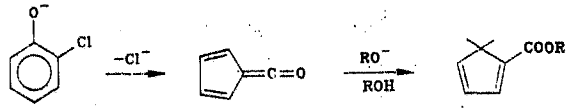
It has not been ruled out in this connection that the photoisomerization of the 2-hydroxypyrylium salts can occur with the preliminary formation of 2-pyrones and their further photoisomerization.

We note that in the ground state of 2-pyrone, as was noted above, $P_{3,6} < 0$ and that cyclization does not take place according to Scheme 5, since $P_{1,3} = 0.063 > 0$. This, along with the small values of the bond orders $P_{1,2}$ (0.325) and $P_{2,3}$ (0.285), suggests the possibility of the thermal conversion of 2-pyrone into furan (see [11]).



In the S_1 state the 1–2 and 2–3 bonds are somewhat strengthened, although they remain the weakest bonds, and the order of the 1–3 bond or, more precisely, the value of $P_{1,3} + K_{1,3}^S$ ($0.063 - 0.215 = -0.152$) becomes negative, forbidding this rearrangement.

The approach under consideration makes it possible to describe photoisomerizations in cases in which the heteroatom is located outside of the ring. As an example, we mention the following reaction [27]:



Of course, the possibility that it takes place with the preliminary elimination of the chlorine atom according to a radical (carbene) mechanism has not been ruled out, but the presence of very large positive long-range bond orders such as $P_{2,6} = 0.237$ and the value $K_{2,6}^S = 0.417$ allow us to postulate photoelectrocyclization at positions 2 to 6 as the first step in this rearrangement.

Thus, the index approach which has been developed for the quantum-chemical description of recylization reactions may be useful for the interpretation not only of dark, but also of some photochemical conversions.

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REACTION OF 5-BROMO-6-AMINO-3-(4-METHYLAMINOBUTYL)PYRIDINE WITH POTASSAMIDE

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F. M. Stoyanovich, and V. G. Granik

UDC 547.822.5'891.2'749.07

It has been found that potassamide reacts with 5-bromo-6-amino-3-(4-methylaminobutyl)pyridine to give a mixture of the starting material, 6-aminonicotine, and 1-methyl-8-amino-2,3,4,5-tetrahydro[4,3-b]azepine. The latter has been obtained independently from 1-methyl-9-cyano-2,3,4,5,7,8-hexahydropyrido[4,3-b]azepin-8-one.

It has previously been shown [1] that the reaction between potassamide and 5-bromo-2-amino-3-(4-methylaminobutyl)pyridine (I) affords a mixture of 2-aminonicotine (II) and 1-methyl-6-amino-2,3,4,5-tetrahydropyrido[4,3-b]azepine (III). However, when the isomeric 5-bromo-6-amino-3-(4-methylaminobutyl)pyridine (IV) was used in this reaction, no reliable data could be obtained for the occurrence of similar heterocyclization reactions [1].

The aim of this investigation was to examine the reaction of the substituted pyridine IV with potassamide, which, as in the case of compound I, could involve an intermediate 3,4-dehydro-compound. The reaction of the pyridine IV with potassamide was carried out under the conditions described in [1]. A mixture of compounds was obtained which proved extremely difficult to separate, and it was not possible to obtain the components of the mixture in the pure state. Consequently, in the initial stages of the investigation attempts were made to synthesize independently 1-methyl-8-amino-2,3,4,5-tetrahydropyrido[4,3-b]azepine (V), which is presumed (by analogy with the findings in [1]) to be a product of the reaction of the pyridine IV with KNH_2. The bicycle V was synthesized as follows: condensation of N-methylcaprolactam diethyl acetal VI with cyanoacetamide afforded the enaminoamide VII, which was cyclized with dimethylformamide diethyl acetal to 1-methyl-9-cyano-2,3,4,5,7,8-hexahydropyrido[4,3-b]azepin-3-one (VIII) [2]. The latter was treated with phosphoryl chloride in the presence of triethylamine hydrochloride (the use of NN-diethylaniline gave much lower yields) to give high yields of the 8-chloro-compound IX, which was reacted with ammonia to give 1-methyl-8-amino-9-cyano-2,3,4,5-tetrahydropyrido[4,3-b]azepine (X). On heating X with polyphosphoric acid, the cyano-group was hydrolyzed followed by decarboxylation to yield the bicycle V.

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