QUANTUM-CHEMICAL INTERPRETATION OF RECYCLIZATION REACTIONS.
7.* ISOELECTRONIC ANALOGS OF THE BENZYL CATION. HETEROFULVENES

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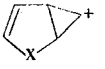
The effect of the nature of the heteroatom, annelation, the position of the methylene group, and the character of the substituent on expansion of the ring of heterofulvene cations was investigated on the basis of the bonded variant of perturbation theory within the framework of the π-electron approach. The rearrangements of 1-methylene-3-oxoisofuran, 2-methylene-3-oxobenzofuran, and N-methyleneisoxazole ylid were also examined. The results of the calculations are in agreement with the experimental data.

In contrast to the recyclization reactions of azabenzyl cations (see [1]), the recyclization reactions of heterofulvene cations, which are isoelectronic heteroanalogs of the benzyl cation (I), cannot be described within the framework of perturbation theory on the basis of calculations of the I cation. Replacement of the —CH=CH— fragment in this cation by a heteroatom that furnishes two π electrons to the system leads to substantial redistribution of the electron density, which affects the orders of both the bonds undergoing cleavage and the newly formed bonds, i.e., ultimately the rate and direction of recyclization, and requires introduction into the computational scheme of the π-electron centers corresponding to these heteroatoms. The aim of the present communication was to develop the suggested approach to the quantum-chemical description of cyclization and recyclization reactions as applied to the rearrangements of a number of five-membered heterocycles.

1. The results of quantum-chemical calculations of 1- and 2-heterofulvene cations are presented in Tables 1 and 2.† It is apparent from the data presented in the tables that one of the long-range bond orders in all of the examined systems is greater than in the benzyl cation (0.283 [1]), which suggests that heterofulvenes undergo rearrangement with greater ease. As in the case of the benzyl cation, two reaction modes are possible: reaction with prior ring opening accompanied by cyclization or reaction with the initial formation of a new bond and subsequent cleavage of one of the old bonds.

The closeness of the long-range orders of the newly formed bonds [$P_{4,6}$ in II (Table 1) and $P_{1,6}$ in X (Table 2)] to the orders of the bonds cleaved in the corresponding structures, as in the case of cation I, indicates that the rearrangements of cations II and X probably proceed through the formation of the same intermediate, viz., bicyclo[3.1.0]-2-hetero-3-hexene (IX):



IX

Subsequent cleavage of the bridge bond in IX should lead to ring expansion to give pyridinium, pyrylium, or thiopyrylium cations, depending on the type of heteroatom. This also evidently explains the indistinguishability of the mass spectra of α- and β-methyl-substituted pyrroles, furans, and thiophenes, respectively [5-10]. Let us also note that the well-known ring ex-

*See [1] for communication 6.
†The parameters of the π-electron Hamiltonian and other details of the calculation were assumed to be the same as those in the description of the UV and NMR spectra of nitrogen- [2], oxygen- [3], and sulfur-containing [4] heterocycles.

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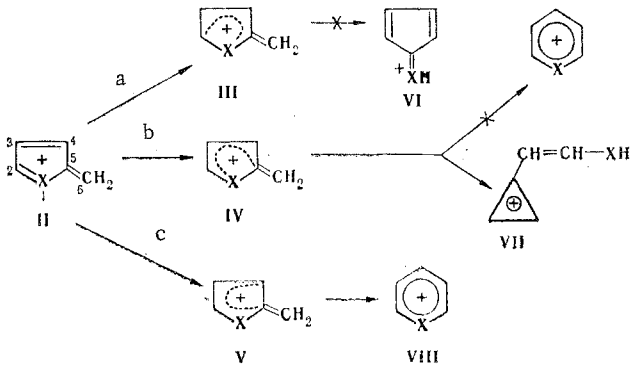
TABLE 1. Reactivity Indexes of 1-Heterofulvene Cations in Recyclization Reactions



Compound*		π-Electron bond orders					
No.	X	$P_{1,5}$	$P_{1,2}$	$P_{4,5}$	$P_{1,6}$	$P_{4,6}$	$P_{2,6}$
II	NH	0,379	0,398	0,482	−0,006	0,328	−0,402
	O	0,338	0,566	0,502	−0,033	0,343	−0,398
	S	0,475	0,734	0,498	0,071	0,308	−0,332
III	NH	0,372	0,122	0,548	−0,242	0,430	−0,382
	O	0,310	0,092	0,558	−0,208	0,416	−0,371
	S	0,391	0,140	0,545	−0,300	0,363	−0,335
IV	NH	0,067	0,597	0,499	0,168	0,211	−0,239
	O	0,062	0,478	0,516	0,126	0,244	−0,268
	S	0,108	0,709	0,536	0,273	0,266	−0,266
V	NH	0,383	0,626	0,117	−0,103	0,267	−0,332
	O	0,334	0,528	0,134	−0,116	0,254	−0,308
	S	0,489	0,851	0,133	−0,064	0,253	−0,262

*The numbering of the atoms in the compounds in all of the schemes does not correspond to the IUPAC nomenclature but was selected for convenience in the discussion of the results of the calculations.

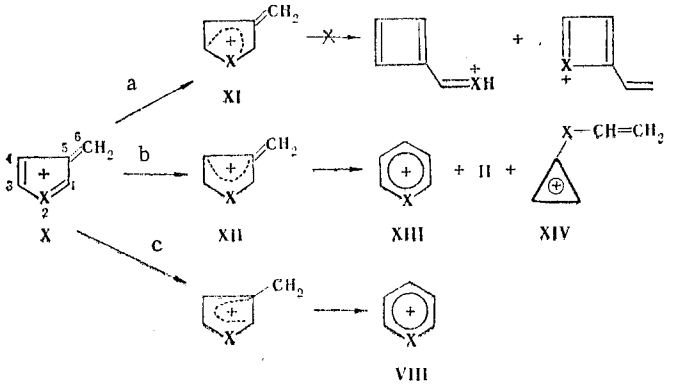
pansion of 2-azabicyclo[3.1.0]-3-hexene [11] to give a pyridine derivative also constitutes evidence in favor of the proposed mechanism. Let us emphasize that, in contrast to the recyclization of the benzyl cation, the rearrangement of the investigated systems was also observed experimentally not only by mass spectrometry but also preparatively [12-15].

The bond orders in II and X differ rather markedly from one another, and for some of the "cleavable" bonds (see Tables 1 and 2) these values are substantially smaller than the analogous orders in the I cation. This should lead to a greater (as compared with the I cation) probability of realization of a rearrangement with prior ring opening. In contrast to [1], we will therefore examine this possibility by calculations within the framework of the scheme of π-acyclic forms currently under development assuming that the corresponding resonance integrals are equal to zero.

The weakest bonds in 1-heterofulvenes II are the 1—5 and 4—5 bonds, which will be cleaved during the reaction. In the case X = NH the 1—2 bond proves to be weaker than the 4—5 bond and also could be cleaved (pathway *a*) with the subsequent formation of VI. This reaction would be similar to the Kost—Sagitullin reaction, which we have previously analyzed thoroughly ([16] and preceding papers), with extension to five-membered heterocycles. However, it follows from Table 1 that in III after cleavage of the 1—2 bond the long-range orders of the 2—6 bonds are greater and more negative, which indicates that this rearrangement is impossible.

Cleavage of the weakest 1—5 bond in II cations (IV) leads to a certain increase in the close-to-zero 1—6 bond order; however, when X = NH, O, it remains less than the long-range 4—6 bond order, i.e., ring expansion via pathway b is unlikely. Rearrangements to give derivatives of cyclopropenyl cation VII are possible in this case [and also for 2-heterofulvenes (see below)]. The presence in the mass spectra and methyl-substituted five-membered heterocycles of peaks with m/z 39, which correspond to the possible products of its fragmentation,

TABLE 2. Reactivity Indexes of 2-Heterofulvene Cations in Recyclization Reactions



Compound		π-Electron bond orders					
No.	X	$P_{2,3}$	$P_{4,5}$	$P_{1,5}$	$P_{4,6}$	$P_{1,6}$	$P_{3,6}$
X	NH	0,458	0,449	0,450	0,171	0,394	−0,195
	O	0,407	0,450	0,527	0,155	0,428	−0,179
	S	0,614	0,473	0,509	0,250	0,344	−0,131
XI	NH	0,079	0,369	0,493	−0,015	0,354	−0,326
	O	0,072	0,366	0,531	−0,023	0,412	−0,311
	S	0,137	0,369	0,551	−0,017	0,400	−0,286
XII	NH	0,404	0,092	0,534	0,259	0,296	0,081
	O	0,356	0,097	0,566	0,244	0,349	0,094
	S	0,517	0,119	0,553	0,253	0,299	0,104
XV	NH	0,444	0,472	0,134	0,086	0,320	−0,333
	O	0,402	0,475	0,159	0,090	0,335	−0,326
	S	0,634	0,512	0,149	0,206	0,296	−0,276

viz., $C_3H_3^+$ cations, evidently may serve as an indirect indication of the formation of cation VII [10].

It is apparent from Table 1 that cleavage of the 4—5 bond (pathway c) should lead to ring expansion, and the reaction products will be the same cations as in the case of recyclization through intermediate IX.

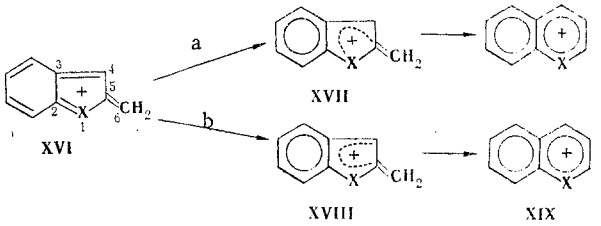
The weakest bonds in 2-heterofulvenes (X) are the 1—5, 2—3, and 4—5 bonds (see Table 2). Cleavage of the 2—3 bond in these compounds (pathway *a*) should have led to the formation of cyclobutadiene derivatives or their heteroanalogs; however, the negativities of the long-range orders of both the 3—6 and 2—6 bonds (for XI $P_{2,6}$ = −0.211, −0.202, and −0.429 when X = NH, O, and S, respectively) constitute evidence that this rearrangement is not realizable.

Cleavage of the 4—5 bond (pathway b, structure XII) leads to a 1.5-fold increase in the long-range orders of the 4—6 bonds (X = NH, O), while the negative orders of the 3—6 bonds become even positive. The formation of a bond between the atoms in the 3 and 6 positions should lead to II, which we examined above. In this case the rearrangement could proceed with retention of the number of atoms in the ring, but the $P_{3,6}$ values are smaller by a factor of three than the $P_{4,6}$ and $P_{1,6}$ values, and this recyclization is therefore unlikely. However, small amounts of products of recyclization of II may evidently be present in the products of rearrangement of X. In XII the long-range orders of the 4—6 bonds are somewhat smaller than the orders of the 1—6 bonds, i.e., derivatives of cyclopropenyl cation XIV, the subsequent fragmentation of which should, as in the case of cations II, lead to $C_3H_3^+$, may also be formed in addition to cations XIII.

It is apparent from Table 2 that cleavage of the 1—5 bond (pathway c) leads to ring expansion, and the reaction products are the same cations as in the case of recyclization through intermediate IX. The certain decrease in the orders of the 1—6 bonds in XV as compared with cations X apparently indicates that the reaction with the initial formation of a new 1—6 bond is preferable.

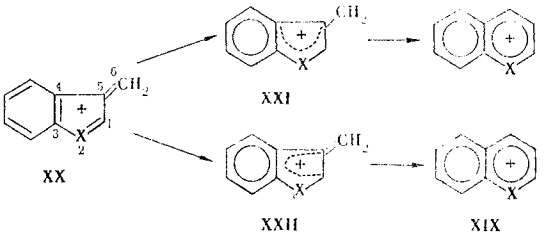
Calculations of the atom—bond mutual polarizabilities for II and X showed that the effect of chemical substitution on the recyclization of these compounds is virtually the same in both

TABLE 3. Reactivity Indexes of Benzo Annelated 1-Heterofulvene Cations in Recyclization Reactions



Compound		π-Electron bond orders			
No.	X	$P_{1,5}$	$P_{4,5}$	$P_{1,6}$	$P_{4,6}$
XVI	NH	0,381	0,508	−0,085	0,391
	O	0,334	0,527	−0,098	0,391
	S	0,458	0,520	−0,081	0,361
XVII	NH	0,049	0,536	0,138	0,273
	O	0,042	0,546	0,093	0,295
	S	0,066	0,558	0,192	0,315
XVIII	NH	0,381	0,121	−0,180	0,266
	O	0,325	0,125	−0,183	0,229
	S	0,458	0,121	−0,216	0,231

TABLE 4. Reactivity Indexes of Benzo Annelated 2-Heterofulvene Cations in Recyclization Reactions

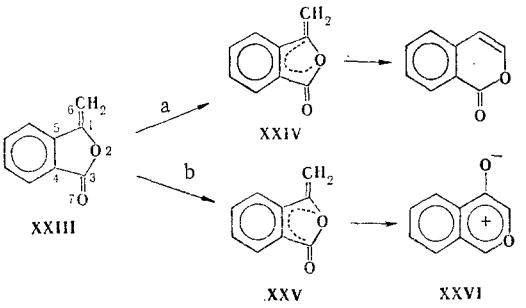


Compound		π-Electron bond orders			
No.	X	P_{1-5}	P_{4-5}	P_{1-6}	P_{4-6}
XX	NH	0,499	0,386	0,358	0,068
	O	0,529	0,387	0,402	0,056
	S	0,516	0,400	0,336	0,107
XXI	NH	0,527	0,052	0,295	0,142
	O	0,557	0,056	0,350	0,133
	S	0,546	0,066	0,298	0,135
XXII	NH	0,088	0,395	0,193	0,002
	O	0,108	0,397	0,207	0,001
	S	0,110	0,415	0,195	0,063

cases. Electron-acceptor substituents in the 3 and 4 positions weaken the 4–5 bonds and have different effects on the 1–5, 1–6, and 4–6 bonds. Thus these functional groups in the 3 position strengthen the first two bonds and weaken the latter bond, whereas the effect of the substituents is just the opposite in the 4 position. Electron-acceptor functional groups in the 6 position strengthen the 4–5, 1–5, and 4–6 bonds and weaken the 1–6 bond, whereas in the 2 position for II and in the 1 position for cations X they weaken both the cleaved and newly formed bonds. The 4–6 bond in X, which is strengthened when electron-acceptor substituents are introduced in the 1 position, constitutes an exception in this case.

2. Annelation of II at the 2–3 bond (structures XVI) and of X at the 3–4 bond (structures XX) has virtually no effect on the strengths of the cleaved 1–5 and 4–5 bonds (compare the data in Tables 1 and 3 and in Tables 2 and 4). In cations XVI the long-range orders of the 4–6 bonds are greater and the long-range orders of the 1–6 bonds are smaller than the corresponding values in II, and ring expansion for this compound should therefore proceed via the same pathway as for cation II. In fact, cleavage of the 1–5 bond in XVI (pathway *a*) leads

TABLE 5. Reactivity Indexes of 1-Methylene-3-oxoisobenzofuran in Reactions Involving Recyclization to 1-Oxoisochromenes



XXIII XXIV XXV XXVI

Compound	π-Electron bond orders			
	$P_{1,2}$	$P_{2,3}$	$P_{2,6}$	$P_{6,7}$
XXIII	0,323	0,333	−0,226	0,111
XXIV	0,008	0,338	0,015	0,093
XXV	0,329	0,009	−0,282	0,099

to an increase in the long-range order of the 1–6 bond (see structure XVII), but it remains smaller than the order of the 4–6 bond, and pathway b will therefore be the more likely pathway of recyclization of XVI with ring expansion. Since the long-range order of the bond decreases somewhat after cleavage of the 4–5 bond in cations XVI, the recyclization of these compounds probably does not proceed through π-open forms XVIII but rather includes a step involving the formation of intermediate benzo derivatives of cations IX. β-Substituted cations XIX should then be obtained as a result of recyclization of 6-substituted cations XVI, which is in agreement with the experimental data [12].

In XX the long-range orders of both the 1–6 and 4–6 bonds are somewhat smaller than for cations X (compare the data in Tables 2 and 4). Nevertheless it is apparent that the basic principles of the recyclization of X should be also retained for benzo derivatives XX. One of them is the more likely initial formation of the 1–6 bond and subsequent cleavage of the 1–5 bond, i.e., rearrangement through intermediate benzo derivatives of cations IX. Precisely recyclization of XVI and XX through the same intermediates evidently leads to the indistinguishability of the mass spectra [7, 17] of α- and β-methyl-substituted indoles, benzofurans, and benzo[b]thiophenes, respectively.

Another annelation mode, viz., at the 3–4 bond, is possible for II. This sort of annelation also has little effect on the orders of the 1–5, 4–5, and 1–6 bonds (the numbering of the atoms in the five-membered ring coincides with that in II), but the long-range orders of the 4–6 bonds decrease by a factor of more than two ($P_{4,6}$ = 0.150, 0.159, and 0.139 for X = NH, O, and S, respectively). A more difficult (than in the other described cases) rearrangement, the products of which would be isoquinoline (X = NH), benzo[c]pyrylium (X = O), and benzo[c]thiopyrylium (X = S) derivatives, should be a consequence of them.

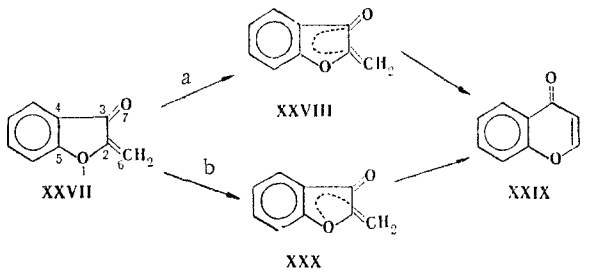
Calculations of the atom–bond mutual polarizabilities for XVI and XX showed that the effect of substituents in the five-membered ring of benzoheterofulvene cations on the rearrangement of the latter is similar to their effect in the nonannelated forms. However, the introduction of functional groups into the benzene ring leads to weak effects.

3. In a number of cases the substituents may participate directly in the rearrangements, and their effect cannot then be taken into account within the framework of perturbation theory, and the π-electron centers of the functional groups must be introduced into the computational scheme to describe the corresponding recyclization reactions.

As an example, let us examine the rearrangements of 1-methylene-3-oxoisobenzofurans to 1-oxoisochromenes and 2-methylene-3-oxobenzofurans to 4-oxochromenes, in which the ketone oxygen atom may be included in the newly formed ring.

The results of calculations of 1-methylene-3-oxoisobenzofuran (XXIII) and its π-acyclic forms are presented in Table 5. The weakest bonds in XXIII are the 1–2 and 2–3 bonds, cleavage of which should lead to different recyclization pathways (pathways *a* and b). The substit-

TABLE 6. Reactivity Indexes of 2-Methylene-3-oxobenzofuran in Reactions Involving Recyclization to 4-Oxochromenes



Compound	π-Electron bond orders			
	$P_{1,2}$	$P_{2,3}$	$P_{3,6}$	$P_{1,6}$
XXVII	0,328	0,316	0,104	−0,227
XXVIII	0,334	0,016	0,026	−0,251
XXX	0,011	0,324	0,065	0,015

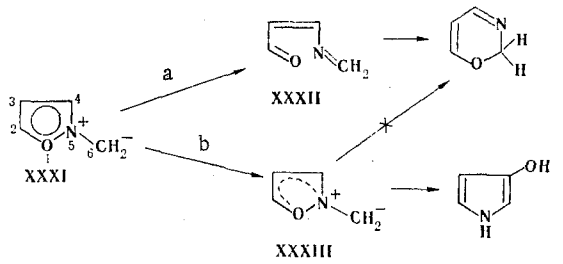
uents in the 6 position have a substantial effect on the direction of rearrangement of this compound. Thus electron-acceptor functional groups markedly weaken the 1—2 bond and strengthen the 2—3 bond ($\pi_{6,1-2} = -0.123$, $\pi_{6,2-3} = 0.022$), and the reaction will therefore be directed along pathway *a*, in agreement with the experimental data in [18]. After cleavage of the 1—2 bond (structure XXIV), subsequent cyclization to 1-oxoisochromenes with the formation of both a new 6—7 and a new 2—6 bond is possible; electron-acceptor substituents in the 6 position strengthen both of these bonds ($\pi_{6,6-7} = 0.020$, $\pi_{6,2-6} = 0.028$). Since $P_{6,7} > P_{2,6}$ for XXIV (see Table 5), the ketone oxygen atom should be included in the newly formed ring with a higher probability.

The effect of electron-donor substituents on the 1—2 and 2—3 bonds in XXIII is just the opposite, i.e., their introduction in the 6 position should lead to substantial strengthening of the 1—2 bond and to a certain weakening of the 2—3 bond. However, the same substituents in the 6 position in π-open form XXV hinder the formation of both the 6—7 and the 2—3 bond ($\pi_{6,6-7} = 0.028$, $\pi_{6,2-3} = 0.017$), i.e., they hinder both the desired and the reverse cyclization. The absence in the literature of experimental data on the rearrangements of XXIII with donor substituents in the 6 position to give derivatives of betaine XXVI is evidently also associated with this.

The orders of the weakest bonds and some of the long-range bond orders (important for recyclization) of 2-methylene-3-oxobenzofuran (XXVII) and its π-acyclic forms are presented in Table 6. After cleavage of the 2—3 bond (pathway *a*), β-substituted chromones XXIX should be formed, while cleavage of the 1—2 bond (pathway b) leads to an α-substituted chromone. In these transformations, in contrast to the rearrangements of XXIII, the ketone oxygen atom is not included in the newly formed ring, since the corresponding long-range bond order is negative ($P_{6,7} = -0.145$ and -0.257 for XXVIII and XXX, respectively). An analysis of the atom—bond mutual polarizabilities shows that the substituents in the 6 position of XXVII have the most substantial effect on the direction of this reaction. Thus electron-acceptor functional groups markedly weaken the 1—2 bond and strengthen the 2—3 bond ($\pi_{6,1-2} = -0.130$, $\pi_{6,2-3} = 0.077$), and when they are present, the reaction should therefore take place primarily via pathway b, in agreement with the available experimental data [18]. The effect of electron-donor substituents is just the opposite, i.e., according to the calculated data, when they are introduced in the 6 position of XXVII, the latter should undergo recyclization via pathway *a*. However, experimental data on such rearrangements are not yet available.

4. It should be borne in mind that in the description of bond cleavage in which an atom that gives two π electrons participates one must take into account the possibility of deviation of the unshared pair of this heteroatom from conjugation. Since it is not always clear which of these pathways (with or without deviation of the unshared pair from conjugation) is realized, one must examine both variants. We have not previously [16] presented data that correspond to deviation of the unshared pair from conjugation, since such calculations gave the same qualitative picture as that obtained without allowance for this fact. A completely

TABLE 7. Reactivity Indexes of N-Methyleneisoxazole Ylid in Rearrangements to 2-H-1,3-Oxazine



Compound	π-Electron bond orders				
	$P_{1,2}$	$P_{1,5}$	$P_{4,5}$	$P_{1,6}$	$P_{2,6}$
XXXI	0,339	0,168	0,548	−0,239	0,414
XXXII	0,903	0,017	0,471	0,220	−0,050
XXXIII	0,305	0,085	0,556	−0,160	0,429

different situation arises in the calculation of N-methyleneisoxazole ylid (XXXI), in which cyclization of the π-acyclic forms with (XXXII) and without (XXXIII) deviation of the unshared pair from conjugation should lead (see Table 7) to two different products. Let us emphasize that because of the low strength of the $O-N^+$ σ bond the probability of deviation of the unshared pair from conjugation with subsequent realization of pathway *a* and the formation of 2-H-1,3-oxazine increases. In fact, this reaction has been observed experimentally [18].

Thus the method developed in this paper describes recyclization reactions not only with ring contraction [19] and retention of the number of atoms in the heteroring [16] but also with ring expansion.

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