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QUANTUM-CHEMICAL INTERPRETATION OF CYCLIZATION AND RECYCLIZATION REACTIONS. 27.* ELECTROCYCLIZATION OF PHENYL DERIVATIVES AND BENZOANNELATED DERIVATIVES OF 1,2,4-TRIAZAHEXA-1,3,5-TRIENE AND 1,2,4-OXADIAZAHEXA-1,3,5-TRIENE

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A theoretical analysis has been carried out of the competing cyclization reactions of 1,2,4-triazahexa-1,3,5-triene and 1,2,4-oxadiazahexa-1,3,5-triene systems using as example C-(arylazo)imines and C-nitrosoimines containing aromatic or aliphatic substituents on the amine nitrogen atom, and also their benzoannelated derivatives.

Keywords: C-(arylazo)imines, 1,2,4-hexatrienes, 1,4-dihydro-1,2,4-benzoxadiazine, 1,4-dihydro-1,2,4-benzotriazine, C-nitrosoimines, 1,2,4-oxadiaza-1,3,5-hexatrienes, 1,2,4-oxadiazoles, 4-phenyl- and 4-alkyl-1,2,4-oxadiaza-1,3-butadienes, 1-phenyl- and 1-alkyl-1,2,4-triaza-1,3-butadienes, 1,2,4-triazole, formazans, formazenes, quantum-chemical calculation, competing reactions, pericyclic reactions, semiempirical methods, sigmatropy, electrocyclization.

C-(Arylazo)imines Ar–N=N–C(R^1)=N–R^2 **1**, C-(azahetarylazo)imines Het–N=N–C(R^1)=N–R^2, and C-nitrosoimines O=N–C(R^1)=N–R^2 **2** attract the attention of chemists because of their high reactivity and the ability to be converted in various ways. The formation of these compounds is occasionally not even established, for example, on oxidation of amidrazones and amidoximes of the type of R^1C(=N–NH–Ar)NH–R^2, R^1C(=N–NH–Het)NH–R^2, and R^1C(=N–OH)NH–R^2 [2-13]. In such reactions, depending on the nature of the substituent at the nitrogen atom of the amide group (R^2 = Ph or R^2 = CH_2R), either derivatives of 1,4-dihydro-1,2,4-benzotriazines are formed [2, 3] (or 1,4-dihydro-1,2,4-benzoxadiazines [4, 5]), or 1,2,4-triazoles [6-11] (or 1,2,4-oxadiazoles [12, 13]). The formation of the indicated compounds is explained by the fact that in the course of the reaction the azoimines **1** and nitrosoimines **2**, having R^2 = Ph, undergo 1,6-electrocyclization of the 1,2,4-triaza(or 1,2,4-oxadiaza)-1,3,5-hexatriene systems (the benzene ring acts as a 5,6-π-fragment of the hexatriene system). In the case of azoimines **1** and nitrosoimines **2**, having R^2 = CH_2R, a 1,5-sigmatropic shift of hydrogen occurs with subsequent 1,5-cyclization by a nucleophilic addition mechanism. In both cases the process is concluded by a stage of oxidative aromatization.

* For Communication 26 see [1] (Part 2 of the series "Theoretical analysis of competing directions of the electrocyclization of 3,4,6-triazaocta-1,3,5,7-tetraene", for Part 1 see [16]).

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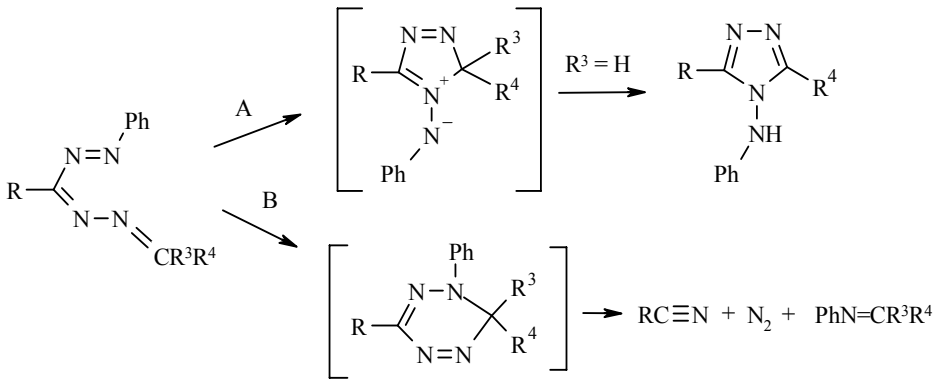
For formazenes (1-aryl-5-ylideneformazans, azoimines **1** with R^2 = N=CR^3R^4) competing 1,6- and 1,5-electrocyclizations are characteristic. In these cases also subsequent pericyclization processes determine the nature of the products formed. These processes are 1,5-electrocyclization and subsequent prototropic shift for aldoformazenes (R^4 = H, Scheme 1, pathway A) and 1,6-electrocyclization and subsequent retro-[2 + 2 + 2] cyclization for ketoformazenes (R^3 and $R^4 \neq$ H) [14, 15] (Scheme 1, pathway B).

Scheme 1



The 1,6-electrocyclization of 1,2,4-triaza-1,3,5-hexatriene and certain problems of the competing cyclization processes of 1,2,4-triaza- and 1,3,4-triaza-1,3,5-hexatriene systems have been considered previously [16]. The problem of the present work is a quantum-chemical analysis of the effect of the nature and position of a substituent (including benzene rings) in 4-R^2-1,2,4-triaza- and 4-R^2-1,2,4-oxadiaza-1,3-butadienes **1** and **2** on the character of the course of pericyclic processes. Unlike the triazahexatrienes considered previously one of the multiple bonds in these compounds is part of an aromatic system.

A combined variant of π-electron theory of excited MO LCAO SSP [17] may serve as the formal apparatus for describing electrocyclization, in the first form of which the index of intramolecular bonding is the bond order between chemically unlinked atoms $P^0_{ik}(0)$.

$$\Delta E = P^0_{ik}(0)\Delta\beta_{ik} \qquad (1)$$

The size of $P^0_{ik}(0)$ characterizes the height of the potential barrier, and the sign indicates the stereospecificity of the reaction (at $P^0_{ik}(0) > 0$ the reaction is disrotatory, at $P^0_{ik}(0) < 0$ conrotatory).

The change in electron distribution under the influence of chemical substitution, as in [18] previously, will be described by the formula:

$$P_{ik}(0) = P^0_{ik}(0) + \pi_{j,ik}\Delta\alpha_j \qquad (2)$$

The presence of functional groups leads to a change in the rate of rearrangement, determined by the size of $\Delta\alpha_j$, characterizing the substituent (their values are tabulated in [19]), and the mutual polarizability $\pi_{j,ik}$ between atom j at the place of introduction of the functional group and the bond ik at which cyclization proceeds.

Rearrangements of C-(arylazo)imines $R^1C(N{=}N{-}Ar){=}N{-}R^2$ **1** and C-nitrosoimines $R^1C(N{=}O){=}N{-}R^2$ **2** are caused by competing pericyclic processes determined primarily by intramolecular bonding in the hexatriene and butadiene fragments containing triaza and oxadiaza fragments. Consequently the subjects of quantum-chemical calculation are the following compounds.

1a	Ph–N=N–C(Ph)=N–Ph	**1f**	Ph–N=N–C(Me)=N–Ph
1b	Ph–N=N–C(Ph)=NH	**2a**	O=N–CH=N–Ph
1c	Ph–N=N–CH=N–Ph	**2b**	O=N–C(Ph)=N–Ph
1d	HN=N–CH=N–Ph	**3a**	Ph–N=N–Py^2
1e	Ph–N=N–CH=NH	**3b**	Ph–N=N–Qu^2

Py^2 = 2-pyridyl, Qu^2 = 2-quinolyl

The numbering of atoms in the conventionally generalized structures (**I-VI**) of the compounds investigated in the work are given in Scheme 2 for convenience and representation of the tabulated data. The numbering of atoms in these structures corresponds to IUPAC nomenclature only for the triaza(or oxadiaza)butadiene fragment, the numbering of atoms in the substituents is arbitrary. For example, at X = N structure **I** corresponds to the $E_{1,2}Z_{2,3}Z_{3,4}$-($E_{N=N}Z_{N-C}Z_{C=N}$) isomer of compounds **1a-f**, **II** to the $E_{1,2}E_{2,3}E_{3,4}$ isomer of azoimine **1a**, and **III** to the $Z_{1,2}Z_{2,3}E_{3,4}$ isomer of azoimine **1a**.

We stress that with the parametrization used previously electrical, diamagnetic, and spectral characteristics have been calculated for a series of five- and six-membered heterocycles (see for example [20]), thermal rearrangements have been described for a series of annelated hexatrienes and polyenes [21, 22], a quantum-chemical interpretation has been given for the Kost–Sagitullin [23, 24] and Elbs [25, 26] reactions, etc.

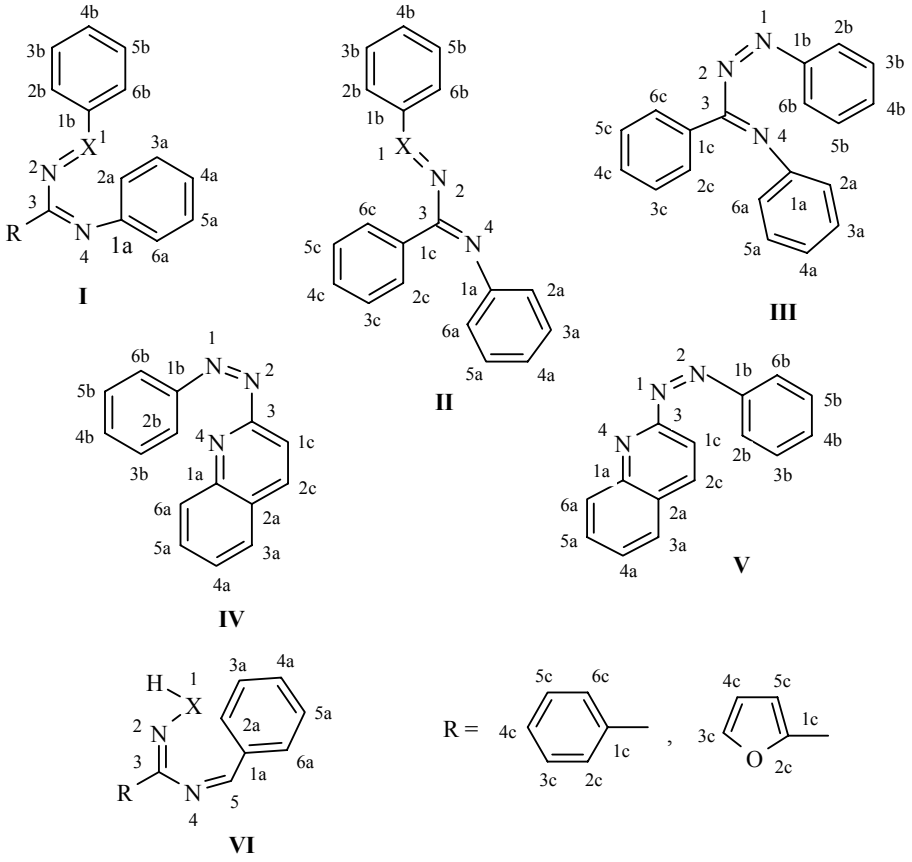
As also in the case of polyenes [21, 22], $P^0_{ik}(0)$ of remote bond orders in compounds **1-3** assume larger positive values only for those pairs of atoms which correspond to the formation of six-membered rings (Table 1). For example, for 1,4-diphenyl-1,2,4-triazabutadiene (**1c**) $P_{1,2a}(0) = 0.1125$, $P_{4,2b}(0) = 0.1101$. At the same time the probability of forming five-membered rings is practically zero: $P_{3,6b}(0) = -0.0094$ and $P_{2,6a}(0) = -0.0160$, although a potential possibility exists for 1,4-electrocyclization by a conrotatory mechanism: $P_{2,2b}(0) = -0.2078$, $P_{3,2a}(0) = -0.2275$. On going over to the $Z_{2,3}Z_{3,4}$ isomer (Scheme 2, **I**, X = N, O) the corresponding values for the remote bond orders are increased even more, i.e. for 1,6-cyclization such a geometry is not only preferred sterically but is more advantageous energetically. Remote bond orders are therefore given in Table 1, and in Table 2 are the mutual polarizabilities $\pi_{j,ik}$ of the systems being investigated in the conformations represented in Scheme 2. The values of $P_{i,j}(0)$ correspond to planar ideal geometry with the least physical distance between the positions *i* and *j*, at which cyclization occurs. For example the data for 1,2a-cyclization correspond to structure **I** ($Z_{2,3}Z_{3,4}$ isomer) in Scheme 2. In contrast to this, when describing

TABLE 1. Remote Bond Orders of Phenyl-substituted 1,2,4-Triaza- and 1-Oxa-2,4-diazabuta-1,3-dienes

Compound	Bond *i,j*	$P_{i,j}(0)$	Compound	Bond *i,j*	$P_{i,j}(0)$
1a	1, 2a	0.1309	**2a**	1, 2a	0.1877
	4, 2b	0.1276			
1b	4, 2b	0.1399	**2b**	1, 2a	0.1770
1c	1, 2a	0.1395	**14**	1, 5	0.1534
	4, 2b	0.1375		3, 6b	0.1018
1d	1, 2a	0.1500	**15**	1, 5	0.1068
1e	4, 2b	0.1478	**16**	1, 5	0.1412
				2, 2a	0.1477
3a	1c, 2b	0.0873	**17**	1, 5	0.0983
	4, 2b	0.0811		2, 2a	0.1513
3b	1c, 2b	0.0693	**18**	1, 5	0.0936
	4, 2b	0.0984		2, 2a	0.1482

4,2b(4,6b) cyclization the planar conformation of the $Z_{1,2}Z_{2,3}E_{3,4}$ isomer is used (structure **III** in Scheme 2). This corresponds to the fact that in these two cases a 1,6-electrocyclization occurs with the participation of carbon atoms of different phenyl substituents.

Scheme 2



Numbering of atoms in compounds **1-3**, **14-18** used in the calculations.
For the example with X = N, the following are depicted: **I** $E_{1,2}Z_{2,3}Z_{3,4}$ isomers of compounds **1a-f**;
II $E_{1,2}E_{2,3}E_{3,4}$ isomer of azoimine **Ia**; **III** $Z_{1,2}Z_{2,3}E_{3,4}$ isomer of azoimine **1a**)

We therefore initially considered the role of the benzene rings, which in the 1,2,4-triaza- (compounds **1a-f**) and 1,2,4-oxadiazabuta-1,3-dienes (compounds **2a,b**) act as substituents and as competing π-fragments of the triaza(or oxadiaza)hexatriene systems. From a comparison of the remote bond orders of azoimine **1c**, unsubstituted in position 3 (R = H), it is evident (see Table 1) that pathway *a* ($P_{1,2a}$ = 0.1395, cyclization of it in the form of the $E_{1,2}Z_{2,3}Z_{3,4}$ isomer **5c**) is somewhat more preferred than pathway *b* ($P_{4,2b}$ = 0.1375, cyclization of it again in the form of the $Z_{1,2}Z_{2,3}E_{3,4}$ isomer **9c**) (Schemes 2 and 3). The introduction into position 3 of a methyl (compound **1f**) or a phenyl (compound **1a**) group reduces both $P_{1,2a}$ and $P_{4,2b}$, however it does not change the conclusion drawn that in these cases 1,2a-cyclization is preferred over 4,2b cyclization. Replacement of the phenylazo group by a nitroso group (i.e. going over to compounds **2a** and **2b**) leads to a significant increase in the remote order of the $P_{1,2a}$ bond, responsible for the passage of 1,6-cyclization (for **2a** $P_{1,2a}$ = 0.1877 and for **2b** $P_{1,2a}$ = 0.1770). On the other hand, if the imine group is a fragment of a pyridine (compound **3a**) or quinoline nucleus (compound **3b**) a significant fall occurs in the corresponding remote bond orders (see structures **IV** and

V of Scheme 2, Table 1). Consequently 1,6-electrocyclization of 2-(arylazo)azacycles must be hampered not only at the imino fragment part of the heterocycle but also at the alternative variant (Scheme 3, pathway *b*), which is confirmed experimentally by the thermal stability of 2-(arylazo)azacycles.

It must be emphasized that, according to the calculations, the more preferred cyclization in ($Z_{N=N}Z_{N=C3}$)-2-(phenylazo)pyridine **3a** is at the C–C bond (at positions 1c and 2b) and not with the participation of the imino fragment of the heterocycle ($P_{1c,2b} = 0.0873 > P_{4,2b} = 0.0811$). Benzoannelation of it at bond 1a-2a (see Scheme 2, structures **IV**, **V**) leads to the reverse order of the values of $P_{i,k}$ ($P_{4,2b} = 0.0984 > P_{1c,2b} = 0.0693$) and cyclization at the C–N bond becomes more preferred. In any case, the remote bond orders are small and it is necessary for the reaction to be activated by the introduction of substituents changing the requisite charge on the ring atoms. We note that in the compounds being considered there are also fairly large (0.0291) orders for the $P_{2,4b}$ and $P_{3,4a}$ bonds, however to effect electrocyclization in this case fission of one of the ring C–C bonds is necessary, which is scarcely probable under the experimental conditions.

Going over to the problem of the influence of substituents on the rate and direction of cyclization, we emphasize that subsequently we will deal exclusively with inductive electronic effects described by mutual atom–bond polarizabilities (see Table 2). In this, no account will be taken of steric effects, which may not be described within the framework of the approach used, and of the effects of the interaction of several substituents between themselves, requiring the application of second order perturbation theory.

As is seen from the values of the mutual polarizabilities $\pi_{j,ik}$ represented in Table 2, 1,6-cyclization of arylazoimines of type **1** with the participation of a nitrogen atom of the azo group and a phenyl ring at the imine group (pathway *a* in Scheme 3) must be significantly activated on introducing donating substituents into positions 4a and 5a of this ring (Scheme 2), and deactivated on introducing these substituents into position 6a. They must be less sensitive to substitution in position 3a. The effects for withdrawing substituents are the opposite.

We note that the nonequivalence of the two *meta* positions 3a and 5a [of the phenyl ring in structure **1** (Scheme 2) adjacent to the imine group and having a substituent in one of these positions] must lead on cyclization of arylazoimines of type **1** to the preferred formation of 3a isomers with donating substituents and 5a isomers with withdrawing substituents (without estimating steric factors). Donating substituents in position 3 deactivate the cyclization reaction and as do substituents in the phenylazo fragment, if they are in the *ortho* and *para* positions of the phenyl group. If they are in the *meta* position they have practically no effect. Electron withdrawing substituents in the positions indicated act in the opposite direction.

Calculation shows that to activate the cyclization reaction by the alternative pathway *b* (Scheme 3) is possible, for example, by introducing donating substituents into position 5b (accelerating the reaction along pathway *b*) and withdrawing substituents into 4a (slowing the reaction along pathway *a* more strongly).

However in the latter case it is necessary to bear in mind that the emergence of phenyl groups from the plane of the molecule (in Table 2 values of $\pi_{j,ik}$ are given corresponding to a planar geometry) leads, as a rule, to some reduction (in the coefficient) of the values of $\pi_{j,ik}$ belonging to this ring.

We note that for C-nitrosoimines **2a,b** it is possible somewhat more effectively to change the rate of cyclization compared with azoimines if substituents are introduced into positions 5a and 6a (for numbering of atoms see Scheme 2) of the N-phenyl ring. Most important in our opinion seems to be the difference of position 3 of nitrosoimines **2**, in which donating substituents (such as a CH_3 group) accelerate 1,2a cyclization but in arylazoimines slow it down.

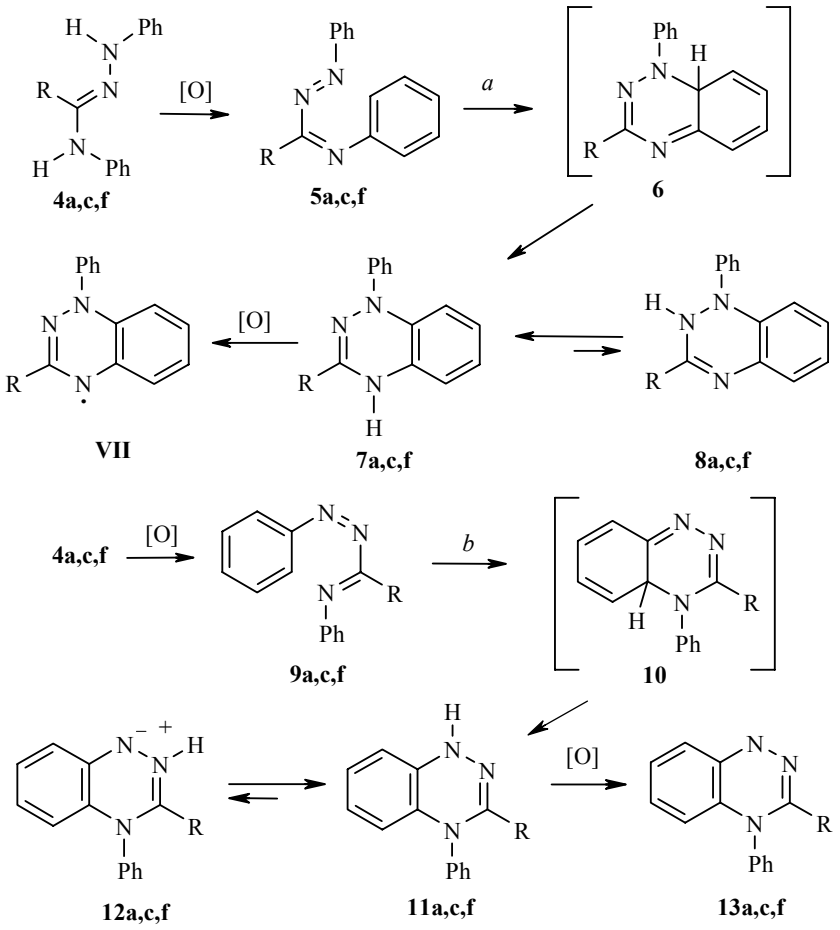
For the possibility of effecting 1,6-electrocyclization of heterylazo compounds **3a** and **3b** with the participation of the ring N atom, it is necessary to activate the reaction with withdrawing substituents in positions 1a (most effective), 2c, or 6b, and with donating substituents in position 5b (Scheme 2). It is necessary to take into account that donating substituents in positions 1a and 2c, which hinder this process, facilitate 1,6-electrocyclization of compounds **3a** and **3b** with the formation of a carbon-carbon bond (1c-2b cyclization). We note that substituents in the benzene ring of the quinoline fragment have practically no effect on the remote bond orders $P_{4,2b}$ and $P_{1c,2b}$.

TABLE 2. Mutual Atom–Bond Polarizabilities ($\times 10^{-2}$ eV^{-1}) in Phenyl-substituted 1,2,4-Triazabuta-1,3-dienes and Their 1-Oxo Analogs (see Scheme 1)

Atom*	Bond												
	1, 2a	4, 2b	4, 2b	1, 2a	4, 2b	1, 2a	4, 2b	4, 2b	1c, 2b	4, 2b	1c, 2b	1, 2a	1, 2a
	1a		**1b**	**1c**		**1d**	**1e**	**3a**		**3b**		**2a**	**2b**
3	—	—	—	0.154	0.268	0.116	0.425	—	—	—	—	-0.135	
1	—	—	—	—	—	0.635	0.211	—	—	—	—	—	—
4			-0.572										
1a								0.280	-0.220				
2a		-0.079			-0.038			-0.038	0.001				
6a	0.056	-0.017		0.088	0.001	0.136				-0.011	0.010	0.282	0.228
3a	-0.033	-0.025		-0.027	-0.013	0.009				0.005	-0.016	-0.016	-0.027
5a	-0.099	0.002		-0.107	0.001	-0.110				0.046	-0.050	-0.231	-0.214
4a	-0.135	-0.045		-0.116	-0.018	-0.067				-0.021	0.005	0.009	-0.029
2b	0.100			0.110									
6b	0.183	0.159	0.185	0.188	0.182		0.211	0.078	0.047	0.103	0.037		
3b	-0.001	0.047	0.046	0.002	0.051		0.054	0.009	0.053	0.019	0.047		
5b	0.031	0.126	-0.158	0.032	-0.128		-0.155	-0.068	-0.013	-0.090	-0.008		
4b	0.126	0.052	0.058	0.135	0.058		0.072	0.002	0.027	0.013	0.029		
1c								0.038		0.038			
2c	0.091	0.111	0.127					0.098	-0.121	0.160	-0.197		0.085
6c	0.003	0.030	0.047										-0.052
3c	0.017	0.018	0.012										0.048
5c	-0.009	-0.008	-0.009										0.011
4c	0.043	0.059	0.066										0.069

* Position of substitution.

Scheme 3



a R = Ph, **c** R = H, **f** R = Me

Competition of 1,2,4-triaza- (pathway *a*) and 1,3,4-triazahexatriene systems (pathway *b*) in electrocyclic reactions of 1,4-diphenyl-3-R-1,2,4-triazabutadienes **1a,c,f** (**5a,c,f; 9a,c,f**).

Since the remote bond orders characterize the height of the potential barrier to cyclization [16, 21, 22], then it is pertinent to use them as indexes of reactivity on kinetic control of the reaction. In the same case, when the barrier to reaction is low, a determining role in the choice of the main reaction pathway is played by the energy characteristics of the products. With the aim of checking both possibilities we have calculated the conjugation energies (*E*) of compounds **7** and **11**, which are the products of 1,6-electrocyclization of diphenyltriazabutadiene (**1c** E_7 = 759.06 and E_{11} = 756.47 kcal/mol), and also their less stable H-tautomers **8** and **12** (E_8 = 748.71 and E_{12} = 729.52 kcal/mol). Consequently direction *a* in Scheme 3 has some preference over direction *b* also on thermodynamic control of the reaction.

Attention is attracted by the fact that as a result of cyclization of compound **1c** (it has two forms **5c** and **9c**) a non-aromatic dihydrotriazine ring is formed (compounds **6** and **10**). The ease of carrying out this process possibly depends mainly on the degree of non-aromaticity of the resulting ring or molecule. Arranging these compounds in a series according to π-electron diamagnetic susceptibility χ^{π} and guided by the π-electron ring currents *I* of the heterocycle (being the magnetic criteria of aromaticity–non-aromaticity [27]), we obtain

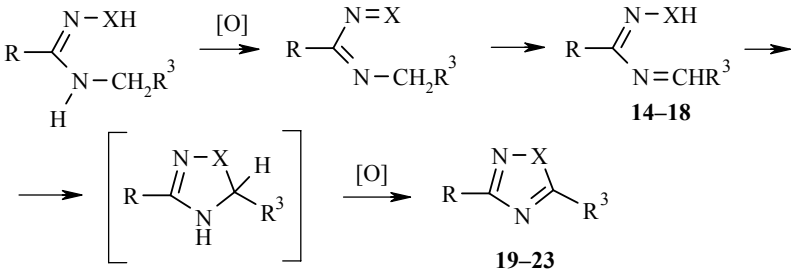
χ^{π}_{8} = 38.10 (I = -0.441) > χ^{π}_{7} = 29.24 (I = -0.646) > χ^{π}_{11} = 28.67 (I = -0.670) > > χ^{π}_{12} = -39.48 (I = -2.158).

If according to conjugation energy (see above) the most energetically favored is structure **7**, and the least is **12**, then according to the magnetic criterion, in contradiction to experiment, the most stable should be structure **8**. This difference is caused by the fact that due to the smallness of the N–N bond order (P_{N-N} = 0.450) structure **8** possesses a reduced nonaromaticity of the dihydrotriazine nucleus. These data illustrate the circumstance that on describing thermodynamic stability it is necessary to use magnetic criteria of aromaticity with care. The values of the ring currents are more linked with the aromatization of compounds **7, 8** and **11, 12** by dehydrogenation: the more paratropic the currents, the more easily will dehydrogenation go.

We note that one further possibility of emerging from a nonaromatic state is homolytic fission of the N–H bond and the formation of the aromatic hyperstable radical **VII** (this radical has already been stored without change for more than 33 years). Its stability is indicated by the increase, compared with the dihydro derivatives **7, 8** and **11, 12,** in the diamagnetic susceptibility χ^{π}_{16} = 62.85 and the induced ring currents in the benzene ring (I = 0.842) of this radical, and also having started with positive current values in the heteronucleus (I = 0.253). The ease of oxidation of dihydrotriazines **7** and **8** into radical **VII** may also be judged by the difference in conjugation energies of these systems, which is approximately 32 kcal/mol greater than for the analogous process involving pyrrole (conversion of pyrrole into a pyrrolyl radical).

The character of the pericyclic process in 4-R-1,2,4-triazabutadienes and 4-R-1-oxa-2,4-diazabutadienes changes sharply if R = CH_2R^1 is introduced in place of the phenyl substituent. In place of 1,6-cyclization in these compounds a 1,5-prototropic shift occurs with subsequent formation of 1,2,4-triazoles or 1,2,4-oxadiazoles [6-13, 28] (Scheme 4).

Scheme 4



14, 19 X = NPh, R = R^3 =H; **15, 20** X = O, R = R^3 = H; **16, 21** X = NPh, R = H, R^3 = Ph;
17, 22 X = O, R = H, R^3 = Ph; **18, 23** X = O, R = 2-furyl, R^3 = Ph

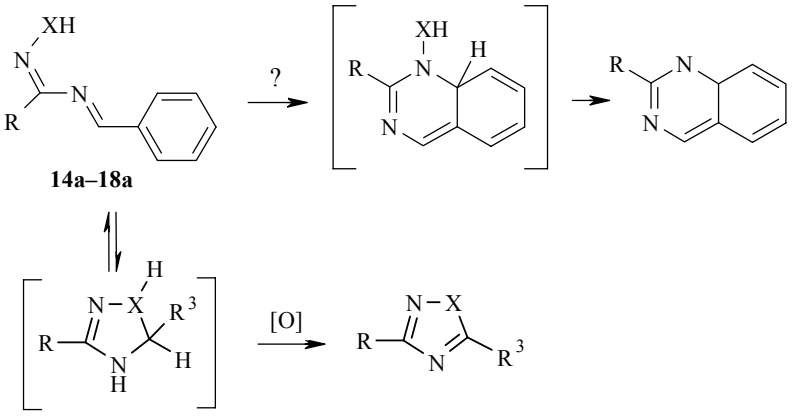
To describe the reactions represented in Scheme 4 we initially estimated the relative C–H acidity of the CH_2 group in compounds **14-18**, resulting after prototropic shift, by the procedure used in describing the Kost–Sagitullin rearrangement [23, 24], the Elbs reaction [25. 26], and others. The residual π-electron charges on the carbon atom of the methylene unit and on the carbon atoms of the imine group were used to assess acidity. Thus from a comparison of the charge on the carbon atom of the imine group in compounds **14** (q_5 = 0.183), **15** (q_5 = 0.200), **16** (q_5 = 0.155), **17** (q_5 = 0.170), **18** (q_5 = 0.176) with the charges on the methylene groups of the anhydrobases [23. 24] (q = -0.18 to -0.27) and dienols [25, 26] (q = −0.09 to –0.13) it is possible to draw the conclusion that the latter possess substantially less C-H acidity than the 4-alkyl analogs of azoimines **1b, 1e**. Consequently the azoimine–ylideneimidrazone and nitrosoimine–ylideneoxime equilibria (Scheme 4) must be displaced strongly to the right (the more so the greater the residual π-electron charge on the CH_2 fragment), which was also observed experimentally [6-9, 12, 13]. The methyl groups in position 3 were substantially unaffected by the size of the charge on the CH_2 group.

We also note that the direction of proton transfer 1–5 corresponds well to the presence of a heteroatom with maximal negative electron charge. We demonstrate this with the charge distribution of the $E_{1,2}E_{2,5}E_{3,4}$ isomers of 4-methylated analogs of the corresponding heterodienes: 4-methyl-1-phenyl-1,2,4-triaza-1,3-butadiene, q_{N1} = -0.074; q_{N2} = -0.046; q_{N4} = 0.248; 4-methyl-1,3-diphenyl-1,2,4-triaza-1,3-butadiene, q_{N1} = -0.064, q_{N2} = -0.052, q_{N4} = 0.266, and 4-methyl-1,2,4-oxadiaza-1,3-butadiene, q_{O1} = -0.153, q_{N2} = 0.005, q_{N4} = 0.284. On analyzing the given data it is possible to draw the conclusion that in all these cases the proton is transferred to the first atom of the triheterobutadiene system (a nitrogen or oxygen atom), which corresponds to a [1,5]-prototropic shift.

On the other hand the 1,5-sigmatropic shift in 1,3-dimethyl-4-phenyl-1,2,4-triazabutadiene CH_3–N=N–C(CH_3)=N–Ph (a prototropic process involving the methyl group in position 1 and the $N_{(4)}$ atom), judging by the size of the charge on the terminal methylene carbon atom CH_2=N–N=C(CH_3)–NH–Ph (q_1 = 0.037 without allowing and q_1 = -0.0140 allowing for the effect of the 3-CH_3 group), must not be effected with such ease.

As follows from the values of the remote bond orders of heterodienes **14-18**, the greatest of which are given in Table 1 (for numbering of the atoms see Scheme 2 structure **VI**), the intramolecular bonding 1-5 with subsequent formation of triazoles (or oxadiazoles) for compounds **16-18** is not solely possible, although the geometry of the tautomerizing ylideneimidrazones and ylideneoximes favors this (the atom−bond polarizabilities are given in Table 3). There is a sufficiently large remote bond order between the nitrogen atom in position 2 and the *ortho* position of the phenyl ring linked with the imine group. In such cases after the formation of a new N–C bond the X–N bond order must fall substantially in the cyclic product (the energy of these bonds is reduced), thereby aiding the elimination of water, at X = O, or aniline, at X = NPh, and the formation of quinazoline derivatives (Scheme 5).

Scheme 5



We were unsuccessful in finding experimental factors indicating the course of such cyclizations. Probably oxidation of the cyclic tautomers of compounds **14a-18a** is more competitive and to obtain quinazoline derivatives it is necessary to use benzylideneamidoximes and benzylideneamidrazones substituted at the atom X (not XH, but XR, R = Alk, Ar, Az, Ts, etc.) or arylideneamidoximes and arylideneamidrazones with appropriate substituents in the phenyl ring of the arylidene fragment. In this case we point out that the substituents aiding cyclization at positions 2,2a and inhibiting cyclization at positions 1,5 must be donating in position 5a and withdrawing in positions 2b and 4b (see Table 3).

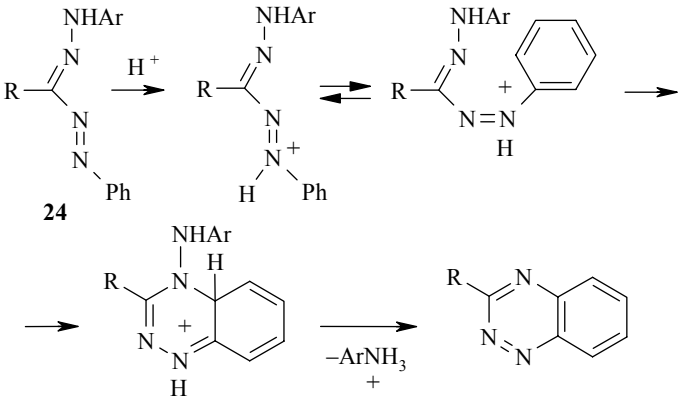
TABLE 3. Mutual Atom–Bond Polarizabilities ($\times 10^{-2}$ eV^{-1}) in N-Ylidenehydrazones and N-Ylideneoximes **14-18**

Atom*	Bond								
	1, 5	3, 6b	1, 5	1, 5	2, 2a	1, 5	2, 2a	1, 5	2, 2a
	14		**15**	**16**		**17**		**18**	
3	0.576		0.238	0.487	0.174	0.195	0.234		
5	1.931	0.303	0.933						
2a				0.304		0.137		0.137	
6a				0.182	0.188	0.093	0.155	0.092	0.124
3a				0.057	0.053	0.008	0.007	0.007	-0.044
5a				0.004	-0.115	-0.009	-0.119	-0.010	-0.140
4a				0.225	0.110	0.080	0.119	0.079	0.196
2b	-0.562	-0.313		-0.529	0.009				
6b	-0.553			-0.547	-0.003				
3b or 3c	-0.040	0.032		-0.042	-0.018			0.025	0.051
5b or 5c	-0.039	-0.137		-0.052	-0.011			0.076	0.012
4b or 4c	-0.453	-0.192		-0.454	-0.022			0.006	-0.001

* Position of substition.

A reaction like the scheme discussed above to form quinazoline derivatives is observed for formazans **24**, which may be considered as 4-azaanalogs of compound **16** [28]. Derivatives of 1,2,4-benzotriazine are obtained in acidic medium from formazans. Probably protonation of the azo group in the formazan fragment facilitates *E-Z* isomerization of this fragment, and also aids 1,6-heterocyclization of the type discussed (Scheme 6).

Scheme 6



The approach developed previously towards a quantum-chemical interpretation of cyclization and recyclization reactions of molecules with conjugated bonds therefore describes well the competing electrocyclizations of derivatives of 1,2,4-triazahexa-1,3,5-triene and 1,2,4-oxadiazahexa-1,3,5-triene, in which the 5-6 double bond is included in an aromatic system.

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