ISSN 1070-4280, Russian Journal of Organic Chemistry, 2015, Vol. 51, No. 2, pp. 245–252. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © V.Yu. Orlov, A.D. Kotov, A.V. Tsivov, A.I. Rusakov, 2015, published in Zhurnal Organicheskoi Khimii, 2015, Vol. 51, No. 2, pp. 255–262.

Mechanism of Formation of 2,1-Benzisoxazoles in Reactions of Nitroarenes with Arylacetonitriles

V. Yu. Orlov, A. D. Kotov, A. V. Tsivov, and A. I. Rusakov

Demidov Yaroslavl State University, ul. Sovetskaya 14, Yaroslavl, 150000 Russia
e-mail: alex_tsivov@mail.ru

Received August 6, 2014

Abstract—Main regularities in reactions of arylacetonitriles with nitroarenes were discussed. The reaction mechanism has been suggested proceeding from the experimental data and the quantum chemical modeling of the limiting stage, the formation of the 2,1-benzisoxazole ring.

DOI: 10.1134/S1070428015020190

The research object of this study is the reaction of nitroarenes with carbanions of arylacetonitriles that depending on the structures of the substrate and the reagent affords different products: from quinone oximes to heterocycles. The reaction of *para*-substituted nitroarenes with arylacetonitriles provide 2,1-benzisoxazoles (anthranils) [1] (Scheme 1, X ≠ H). The reactions of arylacetonitriles with nitroarenes lacking a substituent in the *para*-position [2] (X = H) leads to the formation of arylcyanomethylene-*para*-quinone monooximes.

The mentioned reactions proceed in the media of monohydric aliphatic alcohols in the presence of a large excess (at least two-fold) of sodium or potassium hydroxide. At the use of other solvents or of lesser amounts of alkali metal hydroxide side processes become prevailing (substitution of halogens and the other nucleofuges, hydrolysis of the cyano group, etc.).

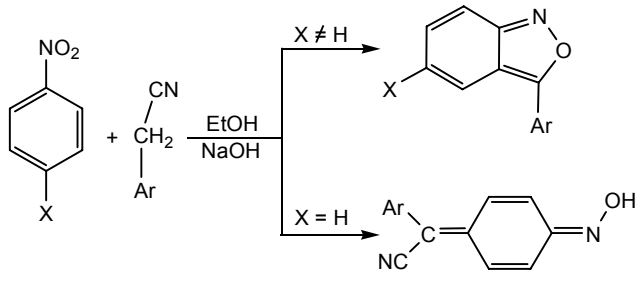
In [3, 4] we investigated the effect of the structures of substrates and reagents on the direction of reactions of mono- and polysubstituted nitrobenzenes, nitroheterocycles, and also dinitroarenes with arylacetonitriles and determined the general structural limitations for substrates and reagents.

Proceeding from the analysis of the data on the study of reactions of *para*-substituted nitroarenes **1** with arylacetonitriles **2** [5, 6] we concluded that the limiting stage in the building up of the final 2,1-benzisoxazoles **3** was the formation of σ^H-complexes **A** (Scheme 2).

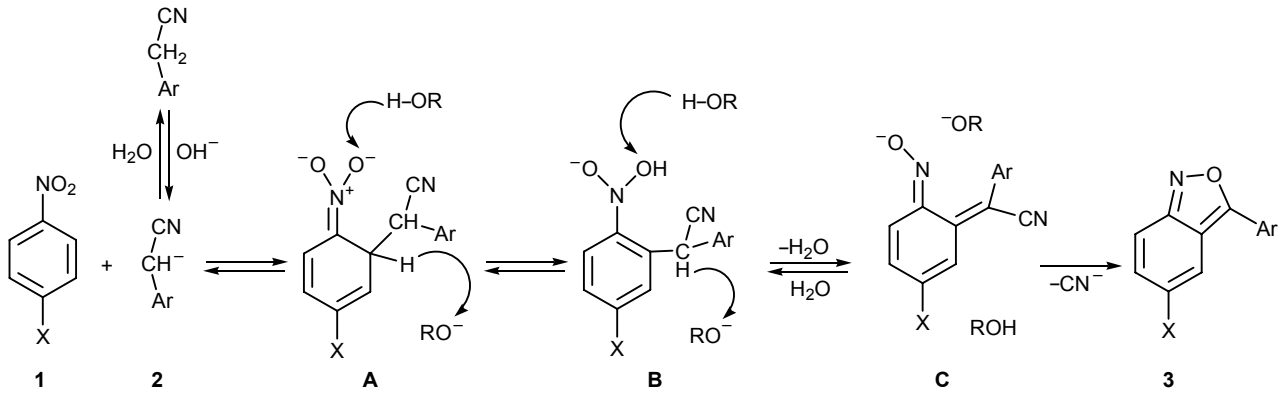
However further in the study on the reactions of arylacetonitriles with nitroarenes lacking a substituent in the *para*-position we showed experimentally the reversibility of the formation of arylcyanomethylene-*para*-quinone monooximes [7], isolated in the individual state and characterized by the modern physicochemical analytical methods (^{1}H, IR, and mass spectra) the minor products of the reactions of the *para*-substituted nitroarenes with some arylacetonitriles [8, 9]. All these data made it possible to suggest the reversibility of some stages in the reactions of arylacetonitriles with *para*-substituted nitroarenes involving analogous intermediates **A**–**C**, excluding the last associative cyclization stage and the formation of the final 2,1-benzisoxazoles **3**, and also to revise the problem of the limiting stage of the overall process.

In [10] also treating the problems of the formation of 2,1-benzisoxazoles the mechanism of the cyclization was studied in detail with the help of the quantum chemical modeling. The obtained values of the energy barriers to the cyclization stage allowed suggesting a hypothesis that this stage was limiting and governing the process laws.

Scheme 1.



Scheme 2.



However only a single process was considered at the simulation in [10]: the reaction of 4-nitrochlorobenzene **1a** with phenylacetonitrile **2a** giving 3-phenyl-5-chloro-2,1-benzisoxazole **3a**. Besides the data on the nature of the limiting stage obtained as a result of the simulation had no significant experimental confirmation.

Therefore we report here on a deeper investigation of the target process including both experimental studies and the quantum chemical modeling on a wide range of compounds (with various substituents in the structure of 4-nitrobenzene).

We also analyzed the correlation dependences between calculated and experimental reaction parameters that permitted verification of the assumption on the limiting stage of the reaction.

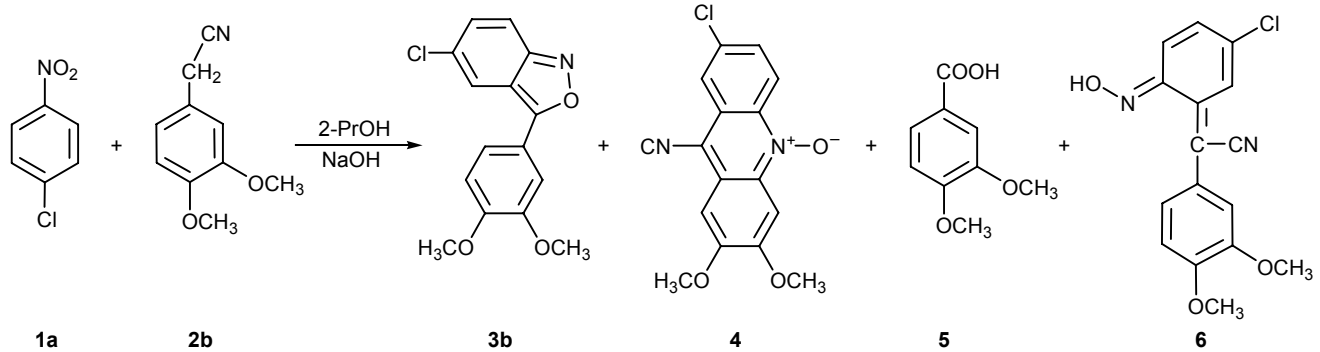
To confirm the existence of the intermediate states involved in the formation of the ring by the transition intermediate **C** → final product **3** we attempted to isolate and characterize the intermediates of reactions of 4-nitrochlorobenzene **1a** with various arylacetonitriles.

In the reaction of 4-nitrochlorobenzene **1a** with 3,4-dimethoxyphenylacetonitrile **2b** in 2-propanol in the presence of a large excess of sodium hydroxide in a nitrogen flow beside the target 3-(3,4-dimethoxyphenyl)-5-chloro-2,1-benzisoxazole **3b**, 9-cyano-10-acridine-*N*-oxide **4**, and 3,4-dimethoxybenzoic acid **5** a bright red crystalline substance was isolated possessing a clear narrow melting point and individual state according to chromatographic data. From the ^{1}H, IR, and mass spectra it was suggested that this compound was a mixture of stereoisomers of *ortho*-quinone oxime corresponding to intermediate **C**, [6-(hydroxyimino)-3-chlorocyclohexa-2,4-dien-1-ylidene]-(3,4-dimethoxyphenyl)acetonitrile **6** (Scheme 3).

Thus we have for the first time experimentally established the existence of intermediate **C** (Scheme 2) and examined its characteristics. This proves that the reaction type under study proceeds through the corresponding *ortho*-quinone monooximes, key intermediate substances in the formation of the 2,1-benzisoxazole ring.

Further aiming to carry out the preliminary identification of the limiting stage we performed the quantum chemical modeling of all stages of the reaction between 4-nitrochlorobenzene **1a** and phenylacetonitrile **2a** leading finally to the formation of 3-phenyl-5-chloro-2,1-benzisoxazole **3a**.

Scheme 3.



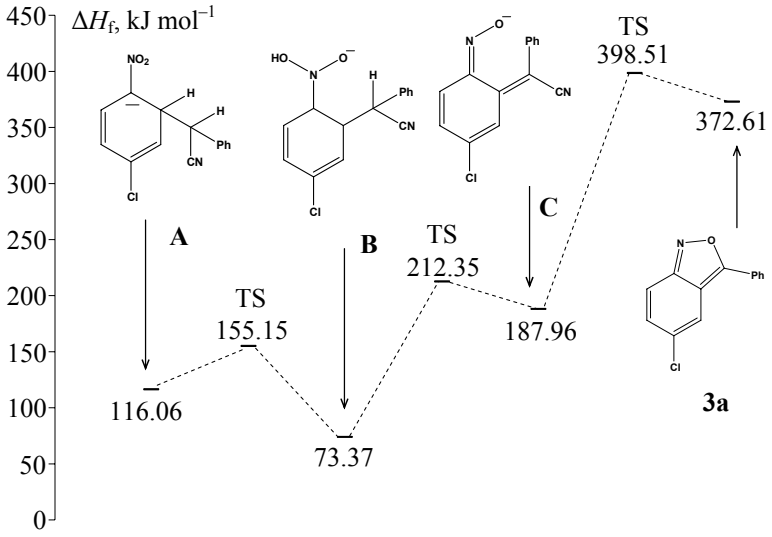


Fig. 1. Energy diagram of the formation of 3-phenyl-5-chloro-2,1-benzisoxazole **3a** (calculation by MOPAC/PM7).

The energy characteristics were calculated for the hypothetical intermediates, the final products, and the transition states. The energy parameters of the intermediates and the transition states are presented in Fig. 1.

The comparison of the obtained energy characteristics shows that the most difficult stage is the latter, namely, the cyclization.

Therefore based on the investigation of the regularities of the target reaction course, on the analysis and interpretation of experimental and published data we suggest in this report the following theoretical model of the studied process (Scheme 2).

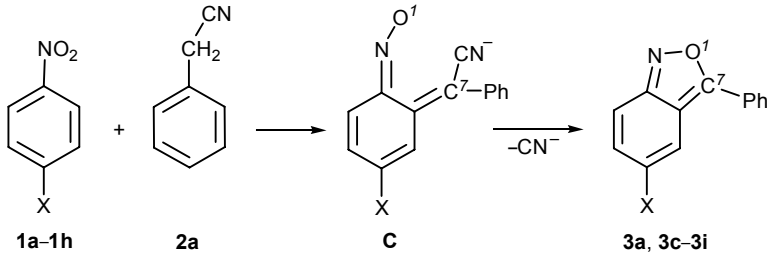
In the first stage the molecule of phenylacetonitrile **2** in the alkaline environment is converted in stable carbanion and further reacts in this form with nitrobenzene **1** giving as a result σ^H-complex **A**.

The second stage consists in the hydrogen transfer on the nitro group involving the solvent thus forming intermediate **B**.

The third stage involves the transfer of the second hydrogen atom to the nitro group with simultaneous water liberation. This results in the ionic form **C** of the reaction product, which in the reaction of arylacetonitriles with nitroarenes without a substituent in the *para*-position to the nitro group leads to the formation of *para*-quinone monooximes, and in the reaction of arylacetonitriles with *para*-substituted nitroarenes by the subsequent cyclization gives 2,1-benzisoxazoles **3** (the fourth stage). According to the assumed theoretical model this stage may be the key (limiting) one leading to the formation of the final 2,1-benzisoxazoles.

Further exploration of the course of the cyclization stage by the transition of intermediate **C** into the final product **3** as the assumed limiting stage of the whole process (Scheme 4) was carried out using the quantum chemical calculations together with the analysis of the obtained experimental data. We performed reactions of 4-X-nitrobenzenes **1a–1h** with phenylacetonitrile **2a** affording 3-phenyl-5-X-2,1-benzisoxazoles **3a** and **3c–3i**.

Scheme 4.



1a–1h **2a** **C** **3a, 3c–3i**

X = Cl (**1a**, **3a**), Br (**1b**, **3c**), Ph (**1c**, **3d**), PhO (**1d**, **3e**), $CH(OCH_2)_2$ (**1e**, **3f**), $MeC(OCH_2)_2$ (**1f**, **3g**), COOH (**1g**, **3h**), 4-$MeC(OCH_2)_2C_6H_4$ (**1h**, **3i**).

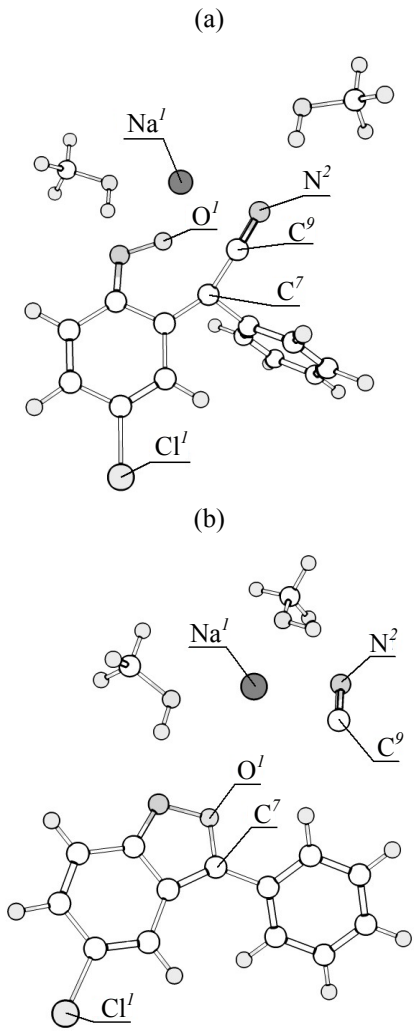


Fig. 2. Geometric configuration of the transition state of cyclization (a) and of the final reaction product (b) **3a** [calculation by PC GAMESS, UHF/6-31G(d,p)].

For accounting for the solvate surrounding we selected the discrete model compatible with UHF (Unrestricted Hartree-Fock) approximation that was realized by the addition of two solvent molecules (alcohol series: methanol–2-propanol). The preliminary calculations showed that the increase in the number of considered solvent molecules did not result in a significant structural and electronic deformation of the initial structure. In order to study the reaction with accounting for the real surrounding the positively charged counterions Na^+ were introduced into the molecular system (Fig. 2).

The simulation of the intramolecular nucleophilic attack during the formation of the 2,1-benzisoxazole rings was performed by gradual rapprochement of the reaction sites, atoms C^7 and O^1, from the distance 3.0 Å corresponding to the source intermediate **C**, to 1.3 Å corresponding to the final product **3**, with the step of 0.1 Å (Scheme 4). At the distance C^7–O^1 1.3–1.5 Å the presumable cleavage of the cyano group C^9N^2 occurs with the subsequent formation of the 2,1-benzisoxazole ring (Fig. 2b).

The structures with the distance 1.9–2.0 Å correspond to the transition state of the studied cyclization stage (Fig. 2a). At the rapprochement of the reaction sites C^7–O^1 to this distance the cyano group C^9N^2 is not yet liberated, and the transition state has the maximum energy on the course along the PES profile (Figs. 3, 4).

The calculation of Hessians for the found transition states of all structures showed that for each TS a single imaginary frequency was present corresponding to the linear vibration of the system along the C^7–O^1 direction that confirmed the correctness of the structure of these TS. Therewith the mentioned C^7–O^1 direction corresponds to the intrinsic reaction coordinate where the change results in the transition of the system "intermediate–final product" from the initial to the final state.

The PES profiles for the transition intermediate **C** → final product **3** constructed as a function of the C^7–O^1 distance and shown in the scale the relative energies E_{rel} are presented in Figs. 3, 4. The calculation was carried out with accounting for the solvation surrounding (model solvent MeOH).

The correlation was examined between the experimentally obtained values of the effective rate constants k_{eff} of the formation of 2,1-benzisoxazoles **3a** and **3c**–**3e** and the calculated values of the energy parameters of the transition states. The parameters selected for the correlation (indices of the reactivity) are the values of the activation barriers in the presumed limiting stage of the formation of 2,1-benzisoxazole rings (Table 1).

A correlation dependence was found of $\ln k_{eff}$ on the values of the activation barriers E_{act} obtained by quantum chemical modeling of the cyclization process (Fig. 5).

For structures **3a** and **3c–3i** a linear correlation was observed between the E_{act} of the formation of 2,1-benzisoxazole rings obtained by quantum chemical modeling and the experimentally found values of the logarithms of the effective rate constants of the reactions between *para*-substituted nitrobenzenes and

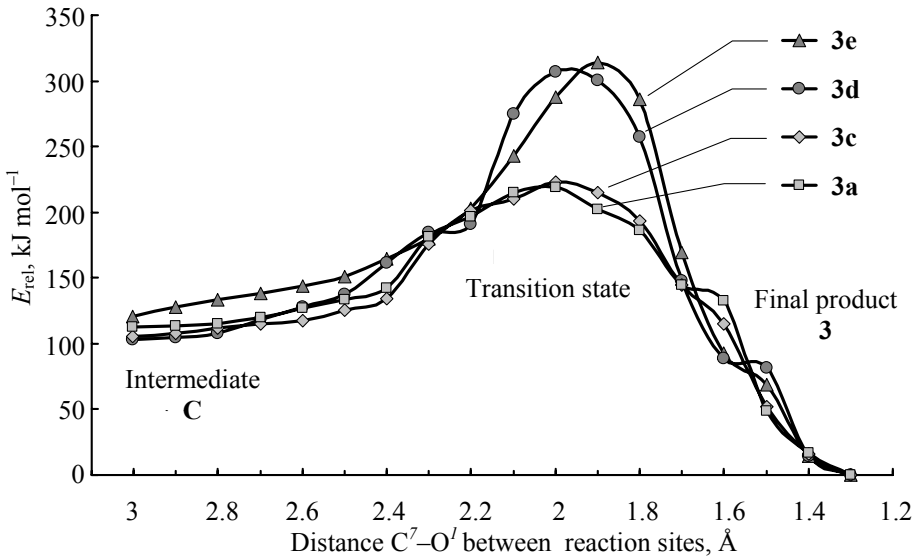


Fig. 3. PES profiles for the transition intermediate **C** → final product **3a** and **3d**–**3e**.

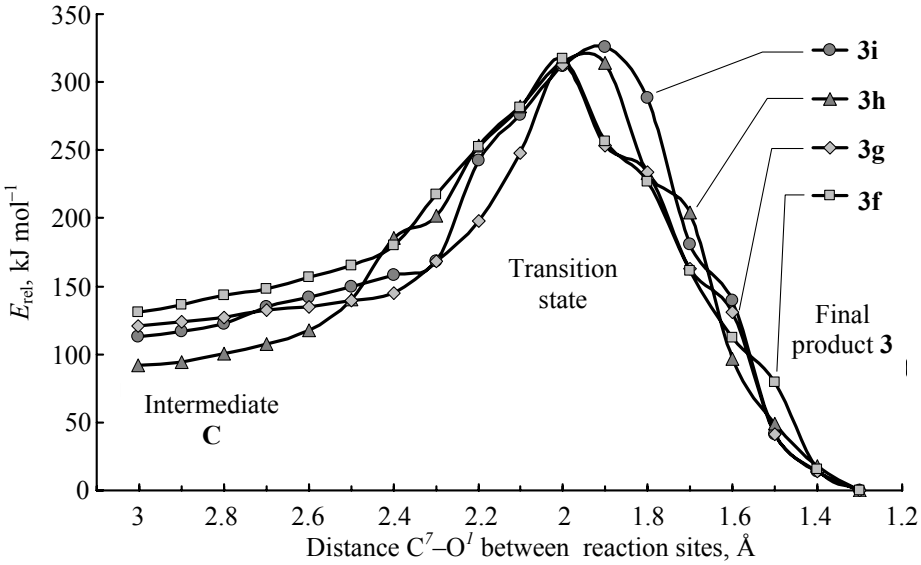


Fig. 4. PES profiles for the transition intermediate **C** → final product **3f**–**3i**.

Table 1. Effective rate constants (k_{eff}) and activation barriers (E_{act}) of the formation of compounds **3a** and **3c**–**3e**, solvent MeOH

Structure	**3a**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**
$k_{eff} \times 10^{-5}$, s^{-1}	26	43	5.5	4.6	5.4	6.4	3.3	2.8
ln k_{eff}	–8.25	–7.75	–9.80	–9.98	–9.82	–9.65	–10.32	–10.48
E_{act}, kJ mol^{-1}	106.61	114.62	203.75	192.91	186.40	188.81	222.82	208.80

the phenylacetonitrile carbanions. The obtained value of the correlation factor (r –0.964) makes it possible to conclude reliably that just the formation of 2,1-benzisoxazole rings is the limiting stage of the reaction.

For the formation of 3-phenyl-5-chloro-2,1-benzisoxazole **3a** the PES profiles for the cyclization process were also constructed characterizing the effect of the applied solvent. A series of lower aliphatic alcohols, like methanol, ethanol, propanol, 2-propanol, buta-

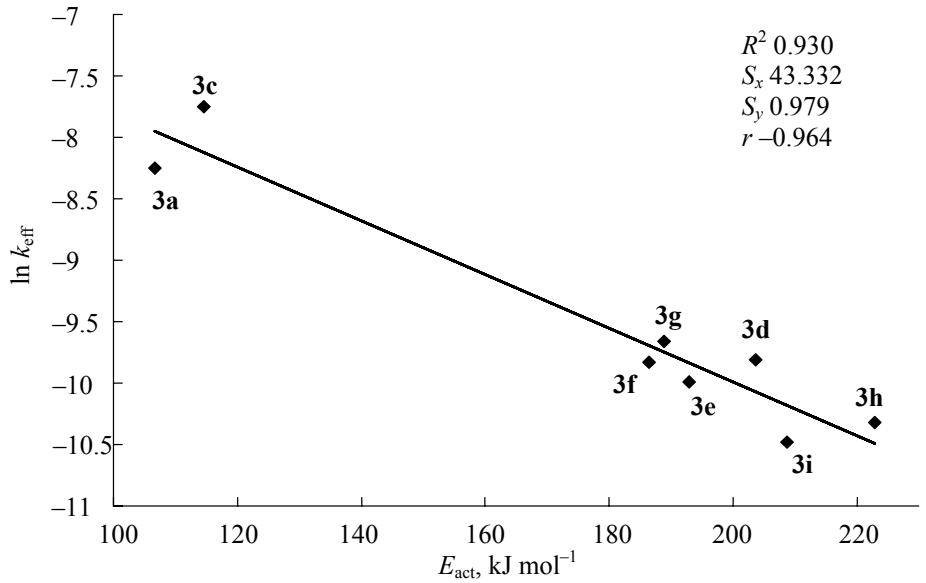


Fig. 5. Dependence of ln k_{eff} on E_{act} for the structures **3a** and **3c–3i** with accounting for solvation (MeOH).

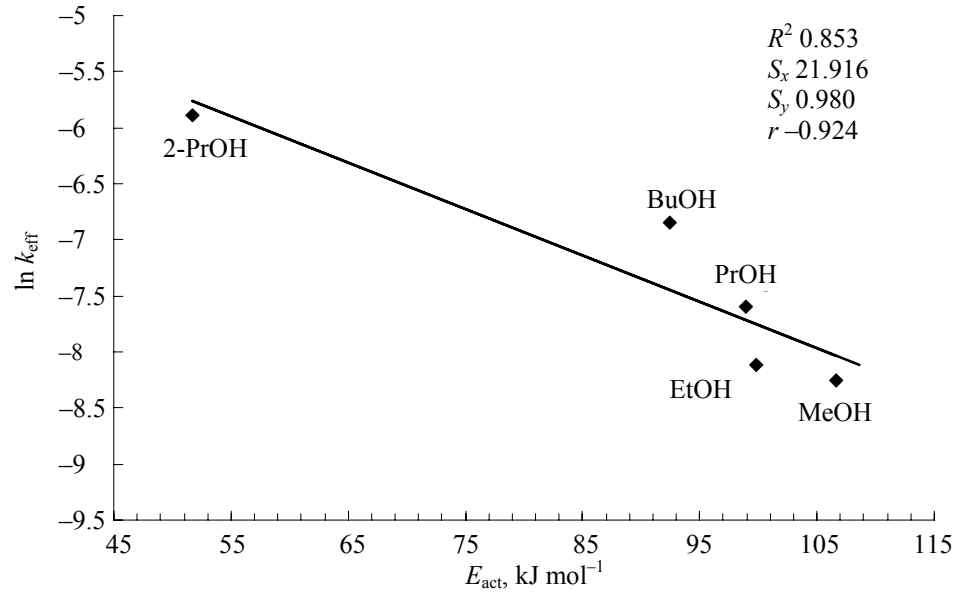


Fig. 6. Dependence of ln k_{eff} on E_{act} for the compound **3a** with accounting for solvation in various solvents.

nol were regarded as solvents. The calculated values of the activation barriers of the studied stage of the chemical reaction are compiled in Table 2. Here the values of the effective constants k_{eff} of the formation of compound **3a** at the use of various solvents are also listed.

The correlation dependence of ln k_{eff} on E_{act} was found for the simulation of the effect of various solvents on the formation of compound **3a** (Fig. 6).

The analysis of the effect of the applied solvent on the course of the target reaction showed that the value of the activation barrier decreased with the increasing polarization of the system. This is expressed in the growing value of the dipole moment of the system "model structure–solvent" in the series MeOH–EtOH–PrOH–BuOH–2-PrOH, and it corresponds to the growing reaction rate. The respective values of the dipole moments of initial structures and transition states for the mentioned solvent series are given in Table 3.

The observed relation also is not contradicting the suggestion of the cyclization as the limiting stage since it proceeds with the cleavage of ionic objects.

Table 2. Effective rate constants (k_{eff}) and activation barriers (E_{act}) of the formation of compound **3a** in various solvents

Solvent	MeOH	EtOH	PrOH	BuOH	2-PrOH
$k_{eff} \times 10^{-5}$, s^{-1}	26	30	50	106	277
ln k_{eff}	–8.25	–8.11	–7.60	–6.84	–5.88
E_{act}, kJ mol^{-1}	106.61	99.85	98.93	92.44	51.75

Table 3. Values of electric dipole moments P of the system compound **3a**–solvent for initial and transition states of cyclization stage

Solvent	MeOH	EtOH	PrOH	BuOH	2-PrOH
P_{in}, D	7.116	8.209	9.772	10.950	11.528
P_{TS}, D	5.842	7.667	7.851	9.471	10.242
$k_{eff} \times 10^{-5}$, s^{-1}	26	30	50	106	277

Thus based on experimental data and quantum chemical calculations we developed in this study a model describing the mechanism of the formation of 3-phenyl-5-X-2,1-benzisoxazoles. The analysis of the correlations of the calculated and experimental reaction parameters allows a conclusion that just the cyclization in the process of the formation of the 2,1-benzisoxazole rings in the reaction of *para*-substituted nitrobenzenes with the carbanion of phenylacetonitrile is the limiting stage governing the main reaction laws.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Bruker Avance AC-300 at operating frequency 300 MHz in DMSO-d_6, Internal reference TMS. IR spectra were recorded on a Fourier spectrophotometer Spectrum 65 from mulls in mineral oil. Mass spectra were measured on an instrument MKh-1310. Melting points were determined on a device PolyTherm A. TLC was carried out on Silufol UV-254 plates, development under UV irradiation or in iodine vapor, eluent hexane–benzene, 3 : 7.

The preliminary quantum chemical modeling of intermediates and transition states was performed using semiempirical method PM7 applying the program MOPAC 2012 [11]. Therewith the search for the transition states was carried out employing the SADDLE procedure (automated search for TS at determined structures corresponding to the initial and final intermediates). The geometry optimization and the calculation of the energy parameters of the studied compounds was performed by the program PC GAMESS/Firefly v. 7.0 [12] using *ab initio* calculation method (Unrestricted Hartree–Fock approximation, parameter SCFTYP=UHF) and the basis set 6-31G(d,p). The geometry optimization was accomplished utilizing the parameter RUNTYP=OPTIMIZE, the Hessian calculation for the structures in question, using RUNTYP=HESSIAN, the search for transition states, RUNTYP=SADPOINT. The visualization of the calculation results was fulfilled with software ChemCraft 1.46 [13].

2,1-Benzisoxazoles. General procedure. Sodium hydroxide and 2-propanol were stirred for 30 min, then arylacetonitrile and nitroaromatic compound were charged in the molar ratio nitroarene–nitrile–NaOH 1 : 1.2 : 10. The reaction mixture was vigoriously stirred at room temperature till the completion of the reaction (TLC monitoring). Then the reaction mixture was poured into water, the separated precipitate was filtered off and washed with water. The filtrate was treated with hydrochloric acid till acidic pH, the separated precipitate was filtered off. The product was purified by recrystallization from an appropriate solvent.

3-Phenyl-5-chloro-2,1-benzisoxazole (3a), mp 113–114°C (ethanol). IR spectrum, ν, cm^{-1}: 1628 (C=N), 1264 (N–O). ^{1}H NMR spectrum, δ, ppm: 7.33 d (1H, H^7), 7.52–7.65 m (3H, $H^{3',4',5'}$), 7.68 d.d (1H, H^6), 8.05 d (1H, H^4), 8.07 d.d (2H, $H^{2',6'}$). Mass spectrum, *m/z* (I_{rel}, %): 229 (72) $[M]^+$, 194 (52), 166 (69), 139 (15), 77 (100), 51 (58).

3-(3,4-Dimethoxyphenyl)-5-chloro-2,1-benzizoxazole (3b), mp 142–144°C (2-propanol). IR spectrum, ν, cm^{-1}: 1634 (C=N), 1265 (N–O). ^{1}H NMR spectrum, δ, ppm: 3.86 s (OCH_3), 7.06 d (2H, $H^{3',5'}$),

7.23 d (1H, H^{7}), 7.54 d.d (1H, H^{6}), 7.89 d (1H, H^{4}), 7.95 d (2H, $H^{2',6'}$). Mass spectrum, *m/z* (I_{rel}, %): 294 (100) $[M]^+$.

5-Bromo-3-phenyl-2,1-benzisoxazole (3c), mp 117–118°C (ethanol). IR spectrum, ν, cm^{-1}: 1626 (C=N), 1264 (N–O). ^1H NMR spectrum, δ, ppm: 7.47 d (H^{7}), 7.55–7.60 m (3H, $H^{3',4',5'}$), 7.62 d.d (1H, H^{6}), 8.08 d.d (2H, $H^{2',6'}$), 8.28 d (1H, H^{4}). Mass spectrum, *m/z* (I_{rel}, %): 275 (40) $[M]^+$, 194 (52), 166 (75), 139 (29), 77 (100), 51 (53).

3,5-Diphenyl-2,1-benzisoxazole (3d), mp 212–215°C (ethanol–DMF). IR spectrum, ν, cm^{-1}: 1630 (C=N), 1264 (N–O). ^1H NMR spectrum, δ, ppm: 7.37 d (1H, H^{7}), 7.42 d.d (1H, H^{6}), 7.45 d (2H, $H^{3',5'}$), 7.67–7.80 m (6H, Ph + $H^{4'}$), 7.82 d (1H, H^{4}), 8.31 d (2H, $H^{2',6'}$). Mass spectrum, *m/z* (I_{rel}, %): 271 (100) $[M]^+$.

3-Phenyl-5-phenoxy-2,1-benzisoxazole (3e), mp 62–65°C (benzene). IR spectrum, ν, cm^{-1}: 1266 (COC), 1633 (C=N). ^1H NMR spectrum, δ, ppm: 7.30 d.d (2H, H^{6}), 7.46 d (2H, H^{4}), 7.50–7.60 m (3H, $H^{3',4',5'}$), 7.72 d (2H, H^{7}), 7.95 d.d (2H, $H^{2',6'}$).

5-(1,3-Dioxolan-2-yl)-3-phenyl-2,1-benzisoxazole (3f), mp 137–138°C (2-propanol). ^1H NMR spectrum, δ, ppm: 4.15 t (4H, CH_2), 5.78 s (1H, CH), 7.40 d (1H, H^{7}), 7.60 d.d (1H, H^{6}), 7.65 m (3H, $H^{3',4',5'}$), 7.96 d (1H, H^{4}), 8.10 d.d (2H, $H^{2',6'}$). Mass spectrum, *m/z* (I_{rel}, %): 267 (63) $[M]^+$, 195 (100), 167 (22), 139 (13), 105 (31), 77 (94), 51 (42).

5-(2-Methyl-1,3-dioxolan-2-yl)-3-phenyl-2,1-benzisoxazole (3g), mp 175–177°C (2-propanol). IR spectrum, ν, cm^{-1}: 1645 (C=N), 1239 (N–O). ^1H NMR spectrum, δ, ppm: 1.61 s (3H, CH_3), 4.02 t (4H, CH_2), 7.44 d (1H, H^{7}), 7.50–7.63 m (3H, $H^{3',4',5'}$), 7.65 d.d (1H, H^{6}), 7.90 d (1H, H^{4}), 8.05 d.d (2H, $H^{2',6'}$). Mass spectrum, *m/z* (I_{rel}, %): 281 (27) $[M]^+$, 266 (100), 222 (31), 194 (12), 166 (21), 139 (10), 105 (19), 87 (31), 77 (55), 51 (21).

3-Phenyl-2,1-benzisoxazole-5-carboxylic acid (3h), mp 248–250°C (AcOH). IR spectrum, ν, cm^{-1}: 2640 (OH), 1704 (C=O). ^1H NMR spectrum, δ, ppm: 7.60 m (3H, $H^{3',4',5'}$), 7.62 d (1H, H^{7}), 7.85 d.d (1H, H^{6}), 8.04 d.d (2H, $H^{2',6'}$), 8.61 d (1H, H^{4}), 13.05 br.s (1H, COOH). Mass spectrum, *m/z* (I_{rel}, %): 239 (100) $[M]^+$, 222 (17), 194 (24), 166 (39), 139 (18), 105 (21), 77 (100), 51 (43).

5-[4-(2-Methyl-1,3-dioxolan-2-yl)phenyl]-3-phenyl-2,1-benzisoxazole (3i), mp 134–136°C (2-propanol). IR spectrum, ν, cm^{-1}: 1630 (C=N). Mass spectrum, *m/z* (I_{rel}, %): 357 (100) $[M]^+$.

[6-(Hydroxyimino)-3-chlorocyclohexa-2,4-dien-1-ylidene](3,4-dimethoxyphenyl)acetonitrile (6), mp 176–178°C (2-propanol). ^1H NMR spectrum, δ, ppm: 3.82 s (6H, OCH_3), 7.02–7.43 m (6H, C_6H_3), 13.18 s (1H, NOH). Mass spectrum, *m/z* (I_{rel}, %): 316 (2.0) $[M]^+$, 289 (67.2), 272 (2.2), 241 (2.1), 210 (8.3), 183 (4.9), 165 (100), 137 (13.7).

The study was carried out under the support of the project no. 178 in the framework of the basic part of the State contract on research for the Demidov Yaroslavl State University.

REFERENCES

1. Davis, R.B., Pizzini, L.C., and Benigni, J.D., *J. Am. Chem. Soc*., 1960, vol. 82, p. 2913.
2. Davis, R.B. and Pizzini, L.C., *J. Org. Chem*., 1960, vol. 25, p. 1884.
3. Orlov, V.Yu., Kotov, A.D., Kopeikin, V.V., Orlova, T.N., Rusakov, A.I., and Mironov, G.S., *Russ. J. Org. Chem*., 1996, vol. 32, p. 1332.
4. Orlov, V.Yu., Kotov, A.D., Sokovikov, Ya.V., and Starikov, A.A., *Russ. J. Org. Chem*., 2000, vol. 36, p. 1735.
5. Orlov, V.Yu., Kotov, A.D., Kopeikin, V.V., Rusakov, A.I., Mironov, G.S., and Bystryakova, E.B., *Russ. J. Org. Chem*., 1998, vol. 34, p. 538.
6. Orlov, V.Yu., Sokovikov, Ya.V., and Kotov, A.D., *Russ. J. Org. Chem*., 2002, vol. 38, p. 100.
7. Konovalova, N.V., Kotov, A.D., Ganzha, V.V., Orlova, T.N., and Orlov, V.Yu., *Izv. Vuzov, Ser. Khim. Khim. Tekhnol*., 2009, vol. 52, p. 59.
8. Orlov, V.Yu., Kotov, A.D., Ganzha, V.V., and Mironov, G.S., *Russ. J. Org. Chem*., 2003, vol. 39, p. 1674.
9. Orlov, V.Yu., Kotov, A.D., and Ganzha, V.V., *Russ. J. Org. Chem*., 2003, vol. 39, p. 1362.
10. Orlov, V.Yu., Kotov, A.D., Tsivov, A.V., and Andreeva, K.V., *Izv. Vuzov, Ser. Khim. Khim. Tekhnol*., 2011, vol. 54, p. 41.
11. *Molecular Orbital Package–MOPAC. http://www.openmopac.net/.*
12. Granovsky, A.A., *Firefly. http://classic.chem.msu.su/gran/gamess/index.html.*
13. *ChemCraft. http://www.chemcraftprog.com/.*