Functional Materials 11, No.1 (2004) © 2004 — Institute for Single Crystals

Experimental and theoretical investigation of the reaction of 2,5-diphenyl-1,3-oxazole and 2,5-diphenyl-1,3,4-oxadiazole dimethylamino derivatives with the Vilsmeier reagent

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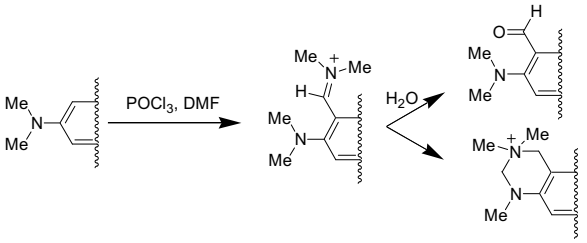
Received May 16, 2003

The 2,5-diphenyl-1,3-oxazole and 2,5-diphenyl-1,3,4-oxadiazole dimethylamino derivatives are widely used as organic luminophores. These compounds are found to be substituted in the *ortho*-position to the dimethylamino group under conditions of the Vilsmeier-Haack reaction. The attack by the $POCl_3$–DMF complex results in formation of the "open" iminium salt which is subjected the isomerization into tetrahydroquinazolinium salt. The substitution reaction directed to the 4 position of the oxazole ring causes formylation. The reactivity of the compounds under investigation and the reaction pathways have been studied using the quantum-chemical semi-empirical methods. The most favorable conditions for synthesis of the quinazolinium salts and aldehydes have been determined. The compounds obtained are of considerable interest as the water soluble high-efficiency luminophores.

Диметиламинозамещенные 2,5-диарил-1,3,4-оксадиазолы и 2,5-диарил-1,3-оксазолы широко применяются в качестве органических люминофоров. Установлено, что в условиях реакции Вильсмайера-Хаака эти соединения замещаются в *орто*-положении к диметиламиногруппе. Атака комплексом $POCl_3$–DMF приводит к образованию "открытой" иминиевой соли, которая затем изомеризуется в тетрагидрохиназолиниевую соль. Реакция замещения, направленная в положение 4 оксазольного цикла, приводит к формилированию. Реакционная способность исследуемых соединений и механизмы реакций исследованы с применением квантово-химических полуэмпирических методов. Определены оптимальные условия синтеза хиназолиниевых солей и альдегидов. Полученные соединения представляют значительный интерес как водорастворимые люминофоры высокой эффективности.

2,5-Diphenyl-1,3-oxazole and 2,5-diphenyl-1,3,4-oxadiazole derivatives, especially those containing dimethylamino group, are known to be high-efficiency luminophores. They are used widely as the laser dyes, light activators for liquid and plastic scintillators, labels and probes for biomedical assays, etc. [1]. Introduction of functional groups into the molecules of the existing luminophores and their further transformation allow to obtain novel compounds having specific properties. One of easy ways to such modification consists in formylation of activated aromatic and heteroaromatic compounds by $POCl_3$–DMF complex (the Vilsmeier-Haack reaction). However, the reaction in *ortho*-position to the tertiary amino group may favor the heterocyclization of the intermediate iminium salt to give tetrahydro-quinazolinium salt instead of the formylation reaction (Scheme 1) [2, 3].



Scheme 1. The two alternative ways to *ortho*-formylation to the dimethylamino group.

The mechanism of the tetrahydro-quinazolinium salt formation was proposed by Meth-Cohn and Taylor for heterocyclization of N,N-dimethyl-4-toluidine [3] and investigated later using semi-empirical quantum-chemical simulation in the example of 4-dimethylamino naphthalic anhydride [4]. According to this mechanism, the reaction begins with the electrophilic substitution including formation of a σ-complex. In the next step, HCl eliminates and the "open" iminium salt **A** is formed (Scheme 2). Then the migration of the dimethylamino group hydrogen atom to the methine carbon occurs followed by cycloisomerisation of the intermediate **B** formed.

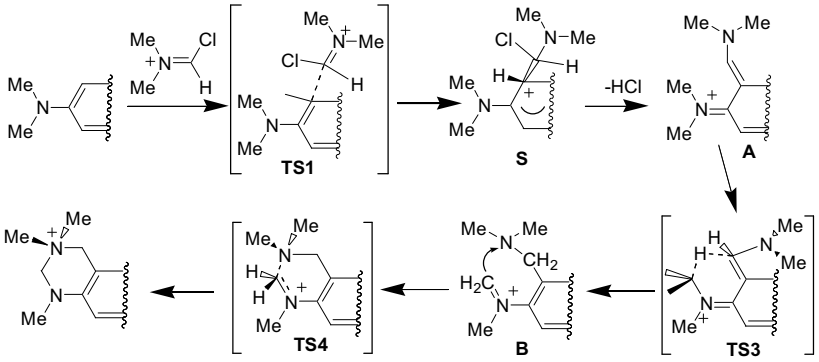
A similar unusual result of the reaction was found previously for N,N-dimethyl-4-toluidine [3], in series of 4-dimethylamino naphthalic and thionaphthalic acid [5, 6], 2,5-diaryl-1,3,4-oxadiazole **1–4** and 2,5-diaryl-1,3-oxazole **5–9** [7] derivatives, and for several other compounds. The cyclic quaternary salts formed are water-soluble luminophores used as fluorescent labels and probes, laser dyes and dyes for polymer materials [5, 6]. 2,5-Diphenyl-1,3,4-oxadiazole **(PPD)**, 2,5-diphenyl-1,3-oxazole **(PPO)**, their alkyl and alkoxy derivatives are known not to react with the Vilsmeier complex [8]. At the same time, the dimethylamino group introduced in *para*-position of the phenyl ring allows the electrophilic attack causing the 1,3-diazinium ring formation [7]. If the dimethylamino group is introduced into the 5-phenyl moiety, formylation in the 4 position of oxazole ring accompanies the heterocyclization (Scheme 3).

In this work, the reactivity and pathways (regioselectivity and ability to the heterocyclization) of the Vilsmeier-Haack reaction in series of 2,5-diaryl-1,3,4-oxadiazoles and 2,5-diaryl-1,3-oxazoles have been studied experimentally and theoretically.

Compounds **1–9** were synthesized using the procedures [9, 10]. The reaction run was monitored by ^{1}H NMR data. ^{1}H NMR spectra were recorded using a Varian Mercury-VX-200 (200 MHz) and a Varian VXP-300 (300 MHz) spectrometers in DMSO–d_6 with HMDS as an internal standard. Quantum-chemical simulations were done by semi-empirical methods CNDO/2 [11], MNDO [12], AM1 [13], and PM3 [14] in their standard parameterizations. Full-geometry optimization was used.

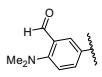
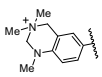
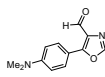
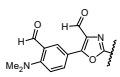
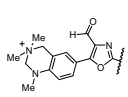
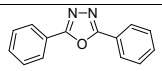
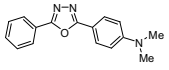
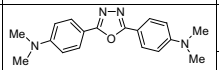
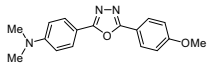
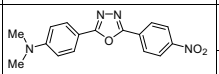
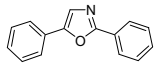
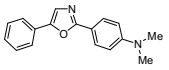
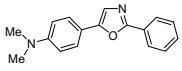
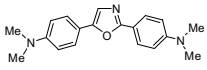
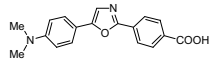
The general procedure for the reaction of dimethylamino derivatives with the Vilsmeier complex is as follows. To a mixture of a dimethylamino derivative **1–8** (0.18 mmol) in DMF (0.5 ml, 6.5 mmol), $POCl_3$ (0.35–1 mmol, 2 equiv.) was added at 60°C and the mixture was heated at 100°C. After the reaction completion, the mixture was treated with water and $LiPF_6$. Data on reaction duration, product content, and synthetic yields are given in Tables 1 and 6.

To investigate the relative reactivity of compounds **1–8**, their interaction with the Vilsmeier complex was provided under identical conditions. To a mixture of a dimethylamino derivative **(1–8)** (0.18 mmol) in DMF (0.5 ml, 6.5 mmol), $POCl_3$ (0.35–1 mmol, 2 equiv.) was added at 60°C and the mixture was heated at 100°C. Then the mixture was treated with water and then $LiPF_6$ was added to convert the water-soluble quinazolinium chloride to insoluble hexafluoro-



Scheme 2. The pathway of tetrahydro-quinazolinium salt formation.

Table 1. The product content and reaction times of the reaction of **1–8** with $POCl_3$–DMF (according to ^1H NMR data).

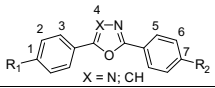
Comp.	Formula	Product content, %						Reaction time, h
		Reactant	 **I**	 **II**	 **III**	 **IV**		
PPD		100	0	0	–	–	–	10
1		81	12	7	–	–	–	1
		0	0	100	–	–	–	4
2		31	24	45	–	–	–	1
		0	0	100	–	–	–	3
3		79	13	8	–	–	–	1
		0	0	100	–	–	–	4
4		84	11	5	–	–	–	1
		0	0	100	–	–	–	4
PPO		100	0	0	0	0	0	10
5		26	28	46	0	0	0	1
		19	13	67	0	0	0	2
		0	0	100	0	0	0	7
6		22	0	7	16	39	16	1
		16	0	10	17	26	31	2
		0	0	0	0	0	100	7
7		17	0	11	16	40	16	1
		8	0	14	10	29	39	2
		0	0	0	0	0	100	4
8		31	0	30	5	20	14	2
		0	0	0	0	0	100	7

phosphate. The precipitate was isolated and analyzed using ^1H NMR. The reaction durations and the product content are collected in the Table 1.

The data presented show that the electrophilic substitution rates estimated by the degree of the reactant disappearance increase in the row: **PPD** ≈ **PPO** < **4** < **1** < **3** < **8** < **2** < **5** ≈ **6** < **7**. Thus, 2,5-diaryl-1,3-oxazoles react faster than analogous 2,5-diaryl-1,3,4-oxadiazoles. The electronic nature of substituent in the 2-phenyl ring influences considerably the substitution reaction rate. For example, introduction of the strong electron-donating dimethylamino group (**2** and **7**) accelerates substitution reaction by 2–3 times while the electron withdrawing groups (**4** and **8**) decelerates it. The displacement of the dimethylamino group from 2-phenyl to 5-phenyl ring accelerates the reaction. Table 1 shows electrophilic attack in oxadiazoles **1–4** and oxazole **5** to proceed towards *ortho* to the dimethylamino group while oxazoles **6–9** are subjected not only to *ortho* substitution but also to formylation in the 4 position of oxazole ring.

To consider theoretically the observed reactivity of **PPD**, **PPO**, **1–9** and their reaction pathways semi-empirical quantum-chemical simulations of the electron struc-

Table 2. Electron charges on the atoms (AM1).



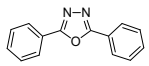
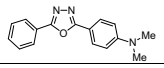
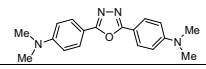
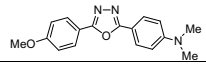
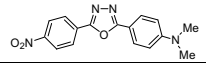
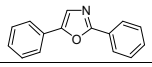
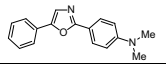
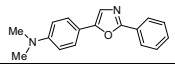
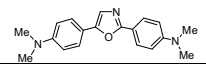
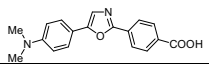
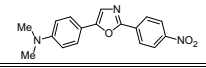
Comp.	Formula	z_1	z_2	z_3	z_4	z_5	z_6	z_7
PPD		−0.106	−0.138	−0.082	–	−0.082	−0.138	−0.106
1		−0.109	−0.138	−0.085	–	−0.040	−0.208	–
2		–	−0.206	−0.044	–	−0.044	−0.206	–
3		–	−0.215	−0.047	–	−0.041	−0.209	–
4		–	−0.073	−0.103	–	−0.032	−0.213	–
PPO		−0.119	−0.130	−0.110	−0.156	−0.085	−0.139	−0.110
5		−0.122	−0.130	−0.112	−0.151	−0.045	−0.207	–
6		–	−0.195	−0.069	−0.173	−0.088	−0.139	−0.113
7		–	−0.194	−0.073	−0.167	−0.048	−0.205	–
8		–	−0.198	−0.065	−0.178	−0.109	−0.079	–
9		–	−0.200	−0.061	−0.181	−0.106	−0.074	–

Table 3. Activation and formation energies of the σ-complexes and "open" iminium salts[1] (PM3)

Compound (position)	ΔG	$\Delta G^{\neq}_{TS1}$	$\Delta\Delta G^{\neq}_{TS1}$	ΔG_{σ}	$\Delta G^{\neq}_{TS2}$	$\Delta\Delta G^{\neq}_{TS2}$	ΔG_A
PPD (2 or 6)	160.66	198.98	38.32	194.66	203.12	42.46	143.32
PPD (1 or 7)	160.66	198.01	37.35	190.98	202.83	42.17	144.59
1(6)	148.30	174.05	25.75	162.29	180.56	32.26	130.22
PPO (6)	141.66	177.96	36.30	171.37	181.62	39.96	122.66
PPO (1)	141.66	174.49	32.83	165.18	177.89	36.23	122.46
PPO (4)	141.66	170.26	28.60	160.67	170.57	28.91	116.72
5 (6)	130.07	154.16	24.09	142.44	160.60	30.53	109.80
5 (4)	130.07	154.04	23.97	144.93	155.85	25.78	102.53
6 (2)	129.96	154.81	24.85	139.55	160.66	30.70	111.08
6 (4)	129.96	149.49	19.53	131.47	152.45	22.49	102.99

[1] The data include the formation energy of the Vilsmeier complex (ΔH = 168.22 kcal·mol^{-1}, ΔS = 0.0828 kcal·mol^{-1}·K^{-1}, ΔG = 138.00 kcal·mol^{-1}).

tures and formation energies (ΔG) of the reactants, intermediates, and products as well as the activation energies ($\Delta G^{\neq}$) for all reaction steps were implemented.

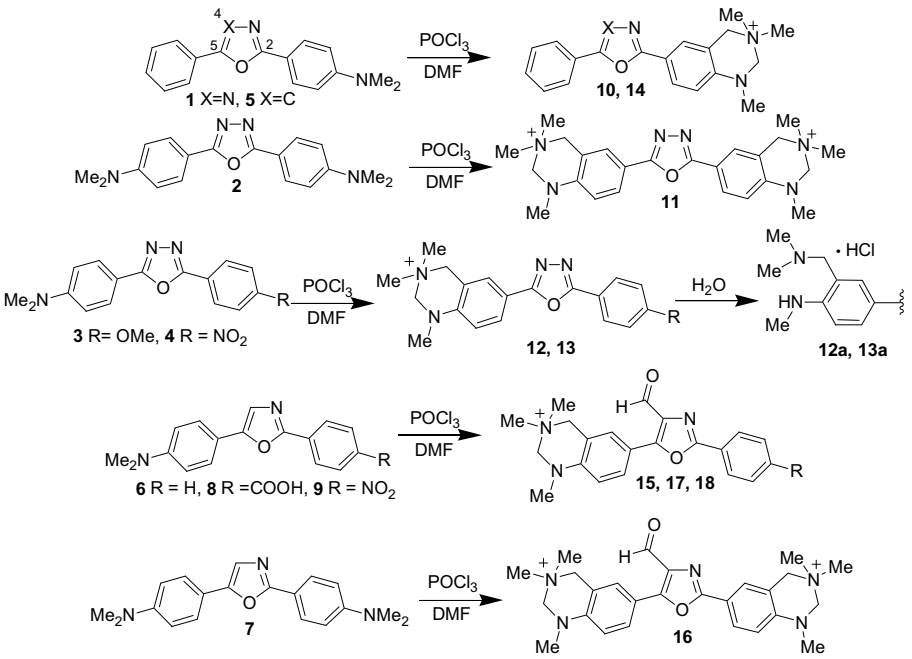
The electrophilic attack direction depends on the negative charge value on the atoms which are able to be substituted. The electron density was calculated using different semiempirical quantum-chemical methods — CNDO/2, MNDO, AM1, and PM3. However, the best agreement between theoretical and experimental dipole moments for the **PPD** and **PPO** molecules was obtained in AM1. The electron charges calculated are presented in the Table 2.

The calculated electron density distributions in the substrate molecules indicate that the highest negative charge in the **PPD** molecule is localized in *meta*-position of the phenyl ring. In the **PPO** molecule, it is the 4 position of the oxazole ring as well as 1 and 6 positions. Introduction of the dimethylamino group in *para*-position of phenyl ring increases substantially the electron density *ortho* thereto. For example, the negative charge on the C6 atom in **1** and **5** increases by 0.070 e. Such result agrees well with experimental data on the substitution direction *ortho* to the dimethylamino group. In compounds **2** and **7** containing dimethylamino groups in both phenyl rings, either *ortho*-position is activated. In fact, the reaction causes the *ortho* substitution to the both dimethylamino groups. In cases of oxazoles **6–9**, containing dimethylamino group in *para*-position of 5-phenyl ring, an increase of the negative charge on the C4 atom also occurs. As a result, the electrophilic substitution in 4 position of the oxazole ring becomes possible.

Under equilibrium conditions, the σ-complex formed in the previous stage is able to be converted to the more stable isomer. That is why to explain the regioselectivity of the substitution reaction under thermodynamically controlled conditions, we compared the activation ($\Delta\Delta G^{\neq}_{TS1}$) and formation ($\Delta G_{\sigma}$) energies of the σ-complexes generated by the different positions (Table 3). The calculations were carried out using the PM3 method, which had been known to be among the better semi-empirical methods for energy calculations [15], particularly for simulations of hydrogen-transfer systems and cyclic transition states [4, 16, 17].

For all investigated molecules, the activation energy of the σ-complex formation ($\Delta\Delta G^{\neq}_{TS1}$) is lower than that for the next stage consisting in HCl cleavage ($\Delta\Delta G^{\neq}_{TS2}$). At the same time, the ΔG_{σ} value is essentially lower than that for the reactants. This is an indication that the first stage is a reversible process. So, the regioselectivity of the substitution reaction depends on the relative stability of the alternative σ-complexes. For example, in the case of **PPD** molecule, the *para*-complex has 4.3 kcal·mol^{-1} lower formation energy than the *meta*-isomer. It means that the *para*-isomer must be the major product of the substitution reaction although the charge distribution predicts favorable attack to the *meta*-position. The low reactivity of **PPD** did not allow us to verify experimentally the above theoretical conclusion. At the same time, the bromination and nitration were found to proceed in the *para*-position of the phenyl ring [18, 19]. As to **PPO** molecule, the lowest ΔG_{σ} has the σ-complex formed in the 4 position of oxazole ring. **PPO** also does not react with the Vilsmeier complex but the electrophilic mercuration [20] by the mercury acetate proceeds in the 4 position of oxazole ring [21].

For the molecule **5**, the σ-complex formed in the 6 position (*ortho*-position to the dimethylamino group) has 2.5 kcal·mol^{-1} lower energy than that in the 4 position of oxazole ring. According to the Boltzmann distribution, the ratio of this two isomeric complexes at the reaction temperature 100°C is 30:1. This calculations agree well with the experimentally found direction of substitution running in the *ortho*-position to the dimethylamino group. In the case of **6**, the complex formed in the 4 position of oxazole ring is 8 kcal·mol^{-1} more preferable. The calculated electron charge distribution and formation energies of the σ-complexes are in good agreement with the experimental results for all investigated compounds. At the next stage, the HCl elimination from the σ-complex occurs and the "open" iminium adduct **A** is generated. The activation energy in this stage ($\Delta\Delta G^{\neq}_{TS2}$) is higher than that of the previous one. That is why just the HCl elimination is the rate-determining step of the substitution reaction (Fig. 1). Table 3 shows that dimethylamino group introduced in the **PPO** and **PPD** molecules (1–9) decreases the $\Delta\Delta G^{\neq}_{TS2}$ by 9–10 kcal·mol^{-1}. As a result, **1–9** react easily with $POCl_3$–DMF complex. If the dimethylamino group is introduced in the 5 phenyl ring (**6**), the decrease of activation energy is more considerable than



Scheme 3. Reactions of 2,5-diaryl-1,3,4-oxadiazole and 2,5-diaryl-1,3-oxazole dimethylamino derivatives with the Vilsmeier reagent.

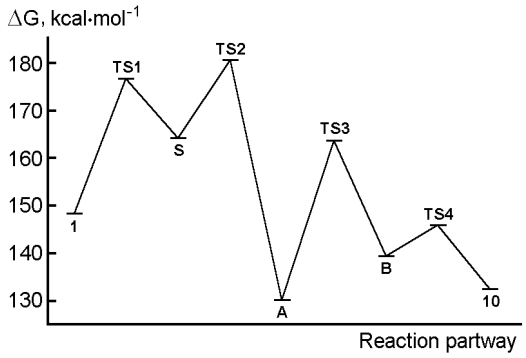


Fig. 1. Energy diagram for the reaction of **1** with the Vilsmeier reagent (PM3).

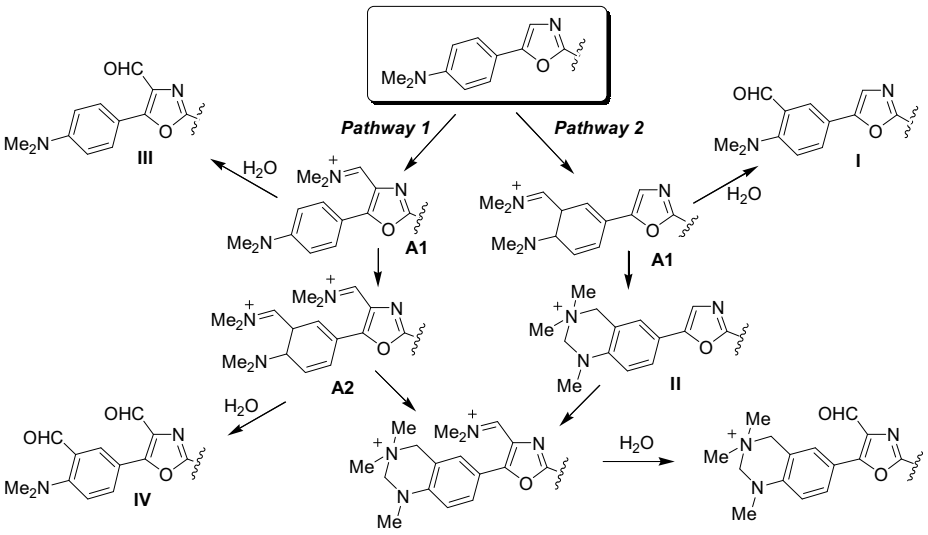
that in the case of 2-(4-dimethylamino)phenyl derivative. This causes the reaction rate to increase. These calculations are in good agreement with experimental relative reactivity data for the investigated compounds (Table 1). As it was mentioned above, the substitution in oxadiazole **1–4** molecules proceeds in the *ortho*-position to dimethylamino group only, while for oxazoles **5–9**, the attack in the 4 position of the heterocycle may accompany the *ortho*-substitution (Scheme 3). The reaction in the 4 position causes only the formylation. This process is known to be kinetically controlled. So, an increased reaction time favors formation of the 4-formyl derivative.

At the same time, the "open" iminium salt formed in *ortho*-position to the dimethylamino group may either be hydrolyzed into aldehyde or be transformed into cyclic quaternary salt. If the isomerisation process is kinetically controlled, the "open" salt **A** is accumulated in the reaction mixture and therefore can be isolated or hydrolyzed into the aldehyde. Thus, in the initial stage of the reaction run, the aldehyde yield is to increase but further heating decreases the aldehyde content and favors heterocyclization.

We have calculated the total reaction pathways for oxadiazole **1** and oxazole **6**. The energy diagram for **1** is presented in Fig. 1 and the energies of the reactants, intermediates, and products are collected in Table 4. The reaction consists of the stages shown in the Scheme 4.

1) Stage **1** → **S**. The molecule **1** is subjected to the electrophilic attack by the Vilsmeier reagent followed by formation of the σ-complex *ortho* to the dimethylamino group. The energy difference between the σ-complex and reactants in this reversible stage is 14 kcal·mol^{-1}. This is an evidence that the equilibrium is shifted towards the reactants.

2) Stage **S** → **A**. The σ-complex eliminate HCl to form the iminium adduct **A**. This step is irreversible due to the highly exothermic ($\Delta\Delta H$ = – 36.65 kcal·mol^{-1}) and irretrievable loss of HCl. The corresponding transition state **TS2** has the highest energy among the other steps of the reaction



Scheme 4. Alternative reaction pathways for 5-(4-dimethylamino)-2-aryl-1,3-oxazoles.

Table 4. Formation energies of the reactants, products and transition states[1] for the reaction **1** → **10** at 100°C (PM3)

Compound	**1**	**TS1**	**S**	**TS2**	**A**	**TS3**	**A**	**TS4**	**10**
ΔG, kcal·mol^{-1}	148.30	174.05	162.29	180.56	130.22	161.67	139.37	145.90	132.48
ΔH, kcal·mol^{-1}	231.70	240.41	225.74	245.72	209.07	240.67	217.06	222.73	207.79
$T\cdot\Delta S$, kcal·mol^{-1}	83.40	66.36	63.44	65.16	78.85	79.00	77.70	76.83	75.31

[1] See note to the Table 3.

1 → **10**. So, this stage is the rate-determining step for the reaction under investigation. Molecular dynamics simulation shows that the system kinetic energy at the reaction temperature 100°C is about 50–55 kcal·mol^{-1} being quite sufficient to provide the reaction.

3) Stage **A** → **B**. The dimethylamino group hydrogen atom is transferred to the methine carbon to give intermediate **B**. The **A** → **B** step has a lower activation energy than the rate-determining step **S** → **A** but it also runs under kinetically controlled conditions because $\Delta\Delta G^{\neq}_{TS3}$ is 31.45 kcal·mol^{-1} while $\Delta G^{\neq}_{TS2}$ is 32.26 kcal·mol^{-1}. These calculations predict that the **A** can be isolated from the reaction mixture. The experimental data in Table 1 show that the reaction mixtures obtained from the oxadiazoles **1**–**4** and oxazole **5** contain 11–28 % of the type **I** aldehydes accompanying the unreacted **1**–**5**. The aldehyde is fading away during the reaction run and totally disappears in 3–7 h. The aldehyde **I** is the native product of the intermediate **A** hydrolysis. The fact of its formation is an additional evidence of the *ortho* substitution to the dimethylamino group.

4) Stage **B** → **10**. The $=CH_2$ group approaches to the dimethylaminomethyl nitrogen atom and the 1,3-diazinium cycle is formed. The low activation energy ($\Delta\Delta G^{\neq}_{TS3}$ = 6.53 kcal·mol^{-1}) in this stage is an indication that the cyclization step runs much faster than the hydrogen transfer process and, therefore, the intermediate salt **B** cannot be detected in the reaction mixture.

Oxazole **6** may react by two ways, starting from the substitution either in the oxazole ring (solid line 1 in Fig. 2) or in the phenyl ring (dash-dotted line 2). The both pathways result in formation of **15a**.

The formation energies of the reactants, intermediates, transition states, and products calculated for the two reaction pathways are presented in the Table 5. The HCl eliminates to form the "open" iminium salt **A** was simulated to be the rate-determining step for the both possible routes. The activation energy for the pathway 1 (82.44 kcal·mol^{-1}) is 5 kcal·mol^{-1} lower than that for the pathway 2 (87.72 kcal·mol^{-1}). Such a difference is quite sufficient to run

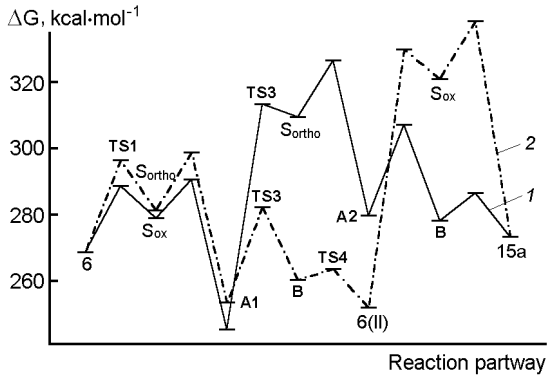


Fig. 2. Energy diagram for the reaction **6** → **15a** (PM3).

Table 5. Formation energies of the reactants, products and transition states[1] in the reaction **6** → **15a** at 100°C (PM3)

Pathway 1		Pathway 2	
Compound	ΔG, kcal·mol^{-1}	Compound	ΔG, kcal·mol^{-1}
6	267.29	**6**	267.29
TS1	287.40	**TS1**	295.05
S(4)	277.60	**S(2)**	280.01
TS2	289.12	**TS2**	297.33
A1	244.05	**A1**	252.11
TS3	313.32	**TS3**	281.01
S(2)	309.47	**A**	259.06
TS4	326.49	**TS4**	262.35
A2	279.64	**6(II)**	250.60
TS5	306.99	**TS5**	329.80
A	278.18	**S(4)**	320.88
TS6	286.49	**TS6**	338.32
15a	273.20	**15a**	273.20

[1] See note to the Table 3.

the reaction preferably by the pathway 1, because the kinetic energy (70–75 kcal·mol^{-1} at 100°C) is 10 to 15 kcal·mol^{-1} lower than the activation energy. This theoretically predicted conclusion is in good agreement with the content of the reaction mixture

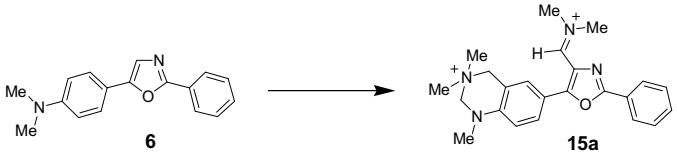
Table 6. Reaction times (t, h) for the reaction of **1–8** with the Vilsmeier reagent and the product yields

Compound	t, h	Yield, %
1I	2	14
10	4	92
2I	1.5–2	27
11	4	95
3I	2	15
12	4	91
4I	2	13
13	4	90
5I	1–1.5	32
14	7	85
6II	2.5	12
6III	2	17
6IV	1.5	42
15	7	80
7II	2–2.5	16
7III	1–1.5	20
7IV	1–1.5	45
16	4	85
8II	2.5	35
8III	3	7
8IV	2.5	25
17	7	80

isolated after heating for 1 h (Table 1, compound **6**, products **6II**, **6III** and **6IV**).

Thus, changing the reaction time, the ratio between the quinazolinium salt and the formylated product **IV** formed in the *ortho*-position to the dimethylamino group can be regulated to favor formation of either of the products. We have used this effect to develop the reasonable synthetic methods for these compounds. The most favorable reaction times providing the highest yields are presented in Table 6.

To conclude, 2,5-diphenyl-1,3-oxazole dimethylamino derivatives react easier with the Vilsmeier reagent than 2,5-diphenyl-1,3,4-oxadiazoles of similar structure. This can be explained by the lower activation energy for the HCl elimination from the σ-complex in the first case. 2-Aryl-5-(4-dimethylamino)phenyl-1,3-oxazoles are formylated in the 4 position of the oxazole ring.



The substitution directed *ortho* to the dimethylamino group in the 2,5-diphenyl-1,3-oxazoles and 2,5-diphenyl-1,3,4-oxadiazoles results in the formation of the "open" iminium salt, which can be either isolated or hydrolyzed to aldehyde. An increased the reaction time favors formation of the cyclic salt. The most favorable reaction times in regard with getting the higher yields of the products have been found.

Acknowledgment. The authors would like to thank Dr.Svetlana V.Iksanova (Institute for Organic Chemistry, NAS of Ukraine) and Dr.Vladimir I.Musatov (Institute for Single Crystals, NAS of Ukraine) who have done ^{1}H NMR measurements. This work was supported by the National Science Foundation (Grant No.0801051062).

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Експериментальне і теоретичне досліження реакцій диметиламінозаміщених 2,5-діарил-1,3-оксазолів та 2,5-діарил-1,3,4-оксадіазолів з комплексом Вільсмайєра

О.М.Семенова, О.С.Галкіна, Л.Д.Паценкер, І.Г.Єрмоленко, І.А.Федюняєва

Диметиламінозаміщені 2,5-діарил-1,3,4-оксадіазоли та 2,5-діарил-1,3-оксазоли широко застосовуються як органічні люмінофори. З'ясовано, що в умовах реакції Вільсмайєра-Хаака ці сполуки піддаються заміщенню в *орто*-положенні до аміногрупи. Атака комплексом $POCl_3$–DMF приводить до утворення "відкритої" імінієвої солі, яка потім ізомеризується в тетрагідрохіназолінієву сіль. Реакція заміщення, спрямована в положення 4 оксазольного циклу, має наслідком формілування. Реакційну здатність сполук, що досліджуються, та механізми реакцій досліджено із застосуванням квантово-хімічних напівемпіричних методів. Визначено оптимальні умови синтезу хіназолінієвих солей та альдегідів. Отримані сполуки є перспективними як водорозчинні люмінофори високої ефективності.