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Semiempirical Calculations in a Search for a Mechanism of 2-Methyl-4-phenylquinoline Formation from 4,4-Diphenyl-3-buten-2-one Oxime Acetate

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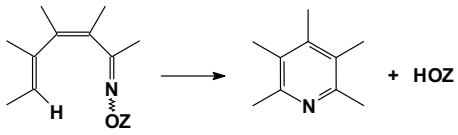
The known thermal non-catalytic formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-3-buten-2-one oxime acetate was analyzed by semiempirical MNDO, AM1 and PM3 methods of calculation, assuming the process consists of three steps: thermal disrotatory electrocyclization of the oxime acetate, inversion of the cyclic intermediate on the nitrogen atom and elimination of acetic acid from the inverted intermediate according to E_i mechanism. It appears from PM3 calculations, which led to better results than MNDO or AM1, that the disrotatory electrocyclization is the rate-determining step for the whole synthesis.

Key words: semiempirical calculations, quinoline, synthesis, mechanism, electrocyclization, inversion, elimination

One can find in the chemical literature several syntheses of six-membered heterocyclic systems [1], often treated in terms of polar reactions despite, that they occur well in non-polar solvents without a catalyst. Particularly, mechanisms of those reactions, which were published before the formulation of the orbital symmetry conservation theory [2], are to be verified. A useful approach to that can be the comparison between calculated and experimental free enthalpies of activation. A careful search through Beilstein Current database [3] brings over one hundred fifty references to syntheses of the pyridine system by formation of nitrogen–carbon bond (Scheme 1). Some of them occur well as thermal processes.

Scheme 1

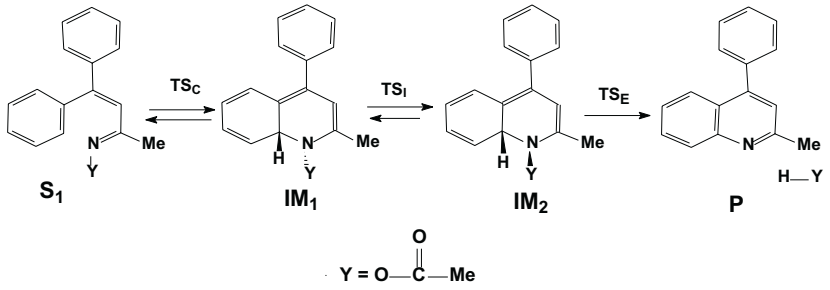


Unfortunately, most of the papers describing syntheses do not contain kinetic data. One of the exceptions is Troszkiewicz synthesis of the quinoline system from oximes of β-phenyl-α,β-unsaturated carbonyl compounds [4,5]. For example, Goszczyński analyzed in details the formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-

3-buten-2-one oxime acetate [6,7]. Carrying out the reaction in hot decaline, he obtained the product in very high yields (over 95%). It enabled kinetic measurements and an estimation of the activation energy being 31.1 kcal/mol for T = 453–463 K or 28.9 kcal/mol for T = 443–453 K. The reaction was treated as the S_E2Ar internal process [6,7]. Under similar conditions (boiling decalin) 4,4-diphenyl-3-buten-2-one oxime without a catalyst did not afford 2-methyl-4-phenylquinoline [7]. This result points out to the importance of *O*-substituent in a starting material. In seventieth we suggested that the first step of the quinoline system formation from 4,4-diphenyl-3-buten-2-one oxime acetate is a thermal disrotatory electrocyclization reaction, followed by elimination of acetic acid from a cyclic intermediate [8].

Until now, the latter mechanistic hypothesis has neither been supported nor denied. Having in hands an efficient tool namely MOPAC 2000 package of programs [9] for semiempirical calculations, we now present some results supporting and supplementing our point of view on the mechanism of the reaction considered. We performed the calculations in the gas phase, assuming that the presence of a non-polar solvent like decalin would not affect the reaction free enthalpy of activation to a larger extent. According to us, the reaction consists of three thermal consecutive steps (Scheme 2): a concerted disrotatory electrocyclization of the starting *syn*-methyl oxime acetate $\mathbf{S_1}$ *via* a cyclic transition state $\mathbf{TS_C}$ and leading to a first bicyclic intermediate $\mathbf{IM_1}$ (dihydroquinoline derivative), inversion on the nitrogen atom in the latter *via* a transition state $\mathbf{TS_I}$ to afford a second intermediate $\mathbf{IM_2}$, and finally a concerted elimination of acetic acid from $\mathbf{IM_2}$ *via* a transition state $\mathbf{TS_E}$ according to E_i mechanism to give products **P** (4-phenyl-2-methyl-quinoline and acetic acid).

Scheme 2



TS_C transition state of electrocyclization step
TS_I transition state of the inversion on nitrogen atom
TS_E transition state of acetic acid elimination from IM_2

CALCULATION PROCEDURES

The calculations were performed on PC computers (Pentium III, 733 MHz) using MOPAC2000 program package [9] with WinMopac 2.0 [10] as a graphic interface. Considering the size, variety of the molecular systems and reactions being the subject of the present study, the choice of a semiempirical method was difficult. Therefore, we performed most of the calculations using three common semiempirical methods (MNDO [11], AM1 [12] and PM3 [13]) and finally compared the calculated results with the experimental data.

At the beginning, structure of the starting material $\mathbf{S_1}$ was optimized with the EF [14] procedure. Then, the reaction path was simulated. The energetic profile of the first reaction step (electrocyclization) was studied (also EF procedure) by changing the distance between the imine nitrogen atom and the carbon atom in one of the *ortho* position of the benzene ring. This finished in obtaining of a local minimum close to $\mathbf{IM_1}$. Changes of the torsion angle O–N–C–H in $\mathbf{IM_1}$ led to a next local minimum close to $\mathbf{IM_2}$. An energetic profile of the third reaction step (elimination) was calculated by changing the distance between the eliminated hydrogen and the doubly bonded oxygen atom in the second intermediate $\mathbf{IM_2}$. Local minima, found at the end of the reaction path for each step, were optimized with the EF procedure to give $\mathbf{IM_1}$, $\mathbf{IM_2}$ and **P**. From the curves obtained we also selected structures close to the expected respective transition states $\mathbf{TS_C}$, $\mathbf{TS_I}$ and $\mathbf{TS_E}$, then optimized them using TS procedure [15], followed by vibrational analysis (FORCE procedure). All the transition states showed only one negative force constant; for the local minima all force constants were positive. The optimized geometries for $\mathbf{S_1}$, $\mathbf{IM_1}$, $\mathbf{IM_2}$ and **P** were used then in appropriate combinations to localize the saddle point by the SADDLE routine [16]. This was done for each elementary reaction ($\mathbf{S_1 \rightarrow IM_1}$, $\mathbf{IM_1 \rightarrow IM_2}$ and $\mathbf{IM_2 \rightarrow P}$), followed by subsequent optimization of $\mathbf{TS_C}$, $\mathbf{TS_I}$ and $\mathbf{TS_E}$ with NLLSQ [17] and TS procedures. At last IRC [18] calculations provided structures associated with the minima very closed to $\mathbf{S_1}$, $\mathbf{IM_1}$, $\mathbf{IM_2}$ or **P**. For the optimized $\mathbf{TS_C}$ structure we also calculated bond orders to find out whether the N–O bond is much weaker in $\mathbf{IM_1}$ than in the starting oxime acetate $\mathbf{S_1}$.

The stationary structures were optimized to a gradient norm always less than 0.01. This was particularly important for proper thermodynamic calculations. Enthalpies and entropies for the stationary structures were calculated using THERMO procedure [19]. These calculations were performed for the gas phase at temperatures up to 500 K. The latter results can be slightly affected by the fact, that the calculations are limited to molecules, which have no internal rotations [19].

For a comparison, similar calculations were also performed for the (hypothetical at 460 K) thermal formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-3-buten-2-one oxime (Y = OH, Scheme 1). In practice, the oxime (in contrast to its acetate) is not converted to 4-phenyl-2-methylquinoline at 460 K without a catalyst [7]. The thermal reaction would require much higher temperature. Results of other supplementary calculations, using similar procedures, are also described.

RESULTS AND DISCUSSION

Some results of our calculations concerning the formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-3-buten-2-one *syn*-methyl oxime acetate in the gas phase at 298 K and 460 K are collected in Tables 1 and 2 respectively. It is worth of mentioning that the reaction-path and the saddle calculations practically led to the same structures of the transition states and their heats of formation. This should be not surprising [20], since the simulated reactions follow the Woodward-Hoffmann symmetry rules [2]. The reaction-path calculations were less time consuming.

Table 1. Results of thermodynamic calculations of 2-methyl-4-phenylquinoline formation from 4,4-diphenyl-3-buten-2-one *syn*-methyl oxime acetate at 298 K.

Stationary structure	method	ΔH_f^o [kcal/mol]	ΔH_f *) [kcal/mol]	Entropy [cal/molK]	ΔG or $\Delta G^{\#}$ [kcal/mol]	$T\Delta S$ or $T\Delta S^{\#}$ [kcal/mol]**)	ΔG or $\Delta G^{\#}$ [kcal/mol]**)
	MNDO	12.953	–	153.9903	–32.946	–	–
S_1	AM1	32.697	–	142.2140	–9.682	–	–
	PM3	29.577	–	159.1760	–17.857	–	–
	MNDO	54.108	41.155	142.3151	11.698	–3.480	+44.644
TS_C	AM1	68.499	35.802	135.9081	27.998	–1.880	+37.680
	PM3	56.029	26.452	148.6455	11.733	–3.138	+29.590
	MNDO	33.650	20.697	142.4143	–8.789	–3.450	+17.578
IM_1	AM1	51.582	18.855	138.2240	–10.391	–1.190	–0.709
	PM3	34.798	5.221	139.5274	–6.781	–5.855	+11.076
	MNDO	43.657	30.704	139.8112	+1.993	–4.225	+34.939
TS_I	AM1	58.469	25.772	137.7754	+17.412	–1.323	+27.094
	PM3	43.057	13.480	139.1901	+1.578	–4.410	+19.435
	MNDO	42.789	29.836	142.2898	+0.387	–3.487	+33.333
IM_2	AM1	52.880	20.183	141.9490	+10.579	–0.079	+20.269
	PM3	39.392	9.816	146.6576	–4.312	–3.730	+13.545
	MNDO	100.046	87.093	140.5115	+58.174	–4.017	+91.120
TS_E	AM1	87.905	55.208	132.3531	+48.464	–2.939	+58.146
	PM3	47.240	17.663	136.6641	+6.514	–6.709	+24.371
	MNDO	–39.544	–52.407	168.5638	–89.776	+4.343	–56.830
P	AM1	–32.448	–52.746	159.3902	–87.042	+5.119	–77.360
	PM3	–41.930	–71.507	155.7942	–88.357	–1.008	–70.500

*)the difference between ΔH_f^o of TS, IM or P and that of S_1.

**)the difference between ΔG of TS, IM or P and that of S_1.

Table 2. Results of thermodynamic calculations of 2-methyl-4-phenylquinoline formation from 4,4-diphenyl-3-buten-2-one *syn*-methyl oxime acetate at 460 K.

Stationary structure	method	ΔH_f^o [kcal/mol]	ΔH_f *) [kcal/mol]	Entropy [cal/mol K]	ΔG or $\Delta G^{\#}$ [kcal/mol]	$T\Delta S$ or $T\Delta S^{\#}$ [kcal/mol]**)	ΔG or $\Delta G^{\#}$ [kcal/mol]**)
	MNDO	27.412	–	192.2300	–61.014	–	
S_1	AM1	47.052	–	180.1643	–35.824	–	
	PM3	44.702	–	199.1858	–46.923	–	
	MNDO	68.171	40.759	179.4857	–14.392	–5.862	+46.622
TS_C	AM1	82.519	35.467	172.9592	+2.958	–3.314	+38.782
	PM3	70.883	26.181	187.9252	–15.563	–5.180	+31.360
	MNDO	47.775	20.363	179.7472	–34.909	–5.742	+26.105
IM_1	AM1	65.710	18.658	175.5567	–32.201	–2.119	+3.823
	PM3	49.643	4.941	178.7738	–32.773	–9.390	+14.150
	MNDO	57.563	30.151	176.5651	–23.657	–7.206	+37.357
TS_I	AM1	72.374	25.322	174.5144	–7.903	–2.599	+27.921
	PM3	57.669	12.967	177.8169	–24.127	–9.830	+22.796
	MNDO	56.967	29.555	179.6667	–25.680	–5.779	+35.334
IM_2	AM1	67.102	20.050	179.5367	–15.485	–0.289	+20.339
	PM3	54.354	9.652	186.2218	–31.308	–5.963	+15.615
	MNDO	114.128	86.716	177.7362	+32.369	–6.667	+93.383
TS_E	AM1	101.921	54.869	169.3832	+24.005	–4.959	+59.829
	PM3	61.798	17.096	175.1411	–18.767	–11.061	+28.156
	MNDO	–24.826	–52.238	211.6753	–122.197	+2.580	–61.183
P	AM1	–17.911	–64.963	197.8387	–108.917	+8.130	–73.093
	PM3	–26.988	–71.690	195.3166	–116.834	–1.780	–69.911

*) the difference between ΔH_f^o of TS, IM or P and that of S_1.
**) the difference between ΔG of TS, IM or P and that of S_1.

As it can be seen from Tables 1 and 2, all three semiempirical methods lead to similar free enthalpies of activation for the electrocyclization and the inversion steps. A dramatic difference can be noticed for the elimination step. While the highest heats of formation and free enthalpies of activation, calculated by MNDO and AM1 methods, refer to the transition states of the elimination step **TS_E**, those calculated by PM3 method refer to the transition state of the electrocyclization step **TS_C**. As we mentioned before, the experimental activation energy for the formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-3-buten-2-one oxime acetate in decalin at 460 K is *circa* 30 kcal/mol [6]. We used it to select the most appropriate semiempirical method. As it can be seen from Table 3, the PM3 model leads to much better results than MNDO or AM1 and gives the free enthalpy of activation surprisingly close to the one calculated from experimental [6] activation energy. From these PM3 calculation results, it can be assumed, that the thermal formation of 2-methyl-4-phenylquinoline from *syn*-methyl 4,4-diphenyl-3-buten-2-one oxime acetate occurs indeed as a three-step process; the first step (namely thermal electrocyclization) being the rate determining one. In accordance with the Woodward-Hoffmann rules [2], the thermal electrocyclization of **S_1** is a disrotatory process, leading to the formation of the bicyclic intermediate **IM_1**, in which two parts of acetic acid to be eliminated (hydro-

gen atom and *N*-acetoxy group) are in a position (close to *anti*-periplanar) unsuitable for the elimination without a catalyst and without an assisting group in the β-position [21].

Table 3. Experimental and calculated ΔH_f, $T\Delta S^{\#}$ and $\Delta G^{\#s}$ for the formation of 2-methyl-4-phenylquinoline from *syn*-methyl 4,4-diphenyl-3-buten-2-one oxime acetate (in decalin or in the gas phase respectively) at 460 K.

$\Delta H^{\#}$; $T\Delta S^{\#}$; $\Delta G^{\#}$ calc. from experimental activation energy [6]	ΔH_f; $T\Delta S^{\#}$; $\Delta G^{\#}$ MNDO calc.*	ΔH_f; $T\Delta S^{\#}$; $\Delta G^{\#}$ AM1 calc.*	ΔH_f; $T\Delta S^{\#}$; $\Delta G^{\#}$ PM3 calc.**
460 K, decalin 30.0; –1.05; 30.5 [kcal/mol]	460 K, gas phase 86.7; –6.667; 93.4 [kcal/mol]	460 K, gas phase 54.8; –4.959; 59.8 [kcal/mol]	460 K, gas phase 26.2; –3.138; 31.4 [kcal/mol]

*) ΔH_f and $\Delta G^{\#}$ calculated as the differences between respective values for $\mathbf{TS_C}$ and $\mathbf{S_1}$

**) ΔH_f and $\Delta G^{\#}$ calculated as the differences between respective values for $\mathbf{TS_E}$ and $\mathbf{S_1}$; in this case heat of formation of $\mathbf{TS_C}$ was higher than that of $\mathbf{TS_E}$.

Fortunately, inversion on the nitrogen atom in this intermediate is a relatively fast reaction (see Table 1 and 2) and leads to another cyclic intermediate $\mathbf{IM_2}$ *via* the transition state $\mathbf{TS_I}$. In the latter intermediate eliminated parts of acetic acid are oriented *syn*-clinal (torsion angle O–N–C–H equal to –63.5°). It is generally accepted that pyrolytic elimination of carboxylic acids from substrates, in which the eliminating groups are oriented *syn*-clinal with respect to each other, involves a six-membered cyclic transition state [21]. Activation energies for such E_i eliminations of acids from alkyl esters are usually quite high and exceed 35–40 kcal/mol, activation entropies being negative (–1 to –11 cal/molK). In the case of $\mathbf{IM_2}$ pyrolysis, the elimination of acid should be easier due to the following reasons. Instead of the strong C–O bond in alkyl esters, the much weaker N–O bond is present in the $\mathbf{IM_2}$; the elimination leads to the very stable aromatic quinoline system. In $\mathbf{TS_E}$ the C–N bond becomes shorter and stronger than in $\mathbf{IM_2}$; the ring containing it partly aromatizes. These facts decrease the free enthalpy of activation of the elimination step. Therefore, the results of PM3 calculations presented here agree with the theory. They support and supplement our earlier suggestions concerning the mechanism of the known formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-3-buten-2-one oxime acetate. What more, calculated (PM3 method) heats of formation for two considered polar structures, that would be intermediates according to S_E2Ar mechanism (Fig. 1), were substantially higher than those of the $\mathbf{TS_C}$. Thus, they should be ruled out from further considerations in vacuum and in non-polar solvents.

We also performed the reaction-path-calculations for the Beckmann rearrangement of the oxime acetate in the gas phase. The rearrangement predominates in the presence of acids, but it has never been observed in non-polar solvents like decalin as a reaction parallel to the formation of 2-methyl-4-phenylquinoline. The calculated (PM3 method) heat of formation for the transition state of the Beckmann rearrangement, in the gas phase at 460 K, equals 105.0 kcal/mol. No wonder, that the Beckmann rearrangement did not accompany the formation of **P** from the oxime acetate $\mathbf{S_1}$.

$\Delta H_{f\,(T = 460\ K)}$ 112 [kcal/mol] $\Delta H_{f\,(T= 460\ K)}$ 66 [kcal/mol]

Figure 1. Heats of formation of hypothetical polar intermediates in the S_E2Ar mechanism of 2-methyl-4-phenylquinoline formation from 4,4-diphenyl-3-buten-2-one oxime acetate at 460 K in the gas phase.

Goszczyński [6] has showed that the *anti*-methyl isomer **S_2** (Scheme 3) of the oxime acetate also undergoes conversion to 2-methyl-4-phenylquinoline in hot decalin. On the ground of macrokinetic measurements, he proved that, in this case, the formation of the quinoline system is preceded by *anti-syn* isomerization (**$S_2 \rightarrow S_1$**) of the oxime acetate.

During this work, the activation parameters for the thermal (460 K) *anti-syn* isomerization of the oxime acetate (**$S_2 \rightarrow S_1$**) were calculated using PM3 method. The heat of **TS_{ISO}** formation (Scheme 2) was found as 83.5 kcal/mol, thus higher than the one of **TS_C** formation at the same temperature. The C–N–O angle in the transition state of the isomerization (**TS_{ISO}**) is close to 175°. This may suggest that the isomerization undergoes by inversion and not by rotation over the double C=N bond. We also attempted to study the electrocyclization of the *anti*-methyl oxime acetate to the cyclic intermediate **IM_2** (Scheme 2). The reaction-path calculations showed that it required more energy to achieve a local minimum than the *anti-syn* isomerization, and finally led *via* a structure similar to **TS_{ISO}**, to the formation of **IM_1** instead of **IM_2**. These results are again in agreement with the experimental observations. Additionally, we ran calculations for a hypothetical thermal formation of 2-methyl-4-phenylquinoline by elimination of water molecule from *syn*-methyl 4,4-diphenyl-3-buten-2-one oxime. Results of the calculations for 460 K are summarized in Table 4. While comparing the data collected in Tables 2 and 4, it becomes clear that an *O*-substituent in the starting material (MeCO in oxime acetate or H in oxime itself) is of secondary importance regarding differences in the calculated heats of formation for the respective transition states of electrocyclization and of inversion on the nitrogen atom. Much greater differences were found for heats of formation of the elimination step transition states.

According to the results of PM3 calculations, the electrocyclization reaction is the rate-determining step for the formation of the quinoline from the oxime acetate. In contrast to that, in the hypothetical thermal conversion of the oxime, elimination of water from the respective cyclic **IM_2** is a slow process, requiring much higher temperatures than 460 K. Not surprisingly then, that the formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-3-buten-2-one oxime at that temperature does not occur without a catalyst [7].

Scheme 3

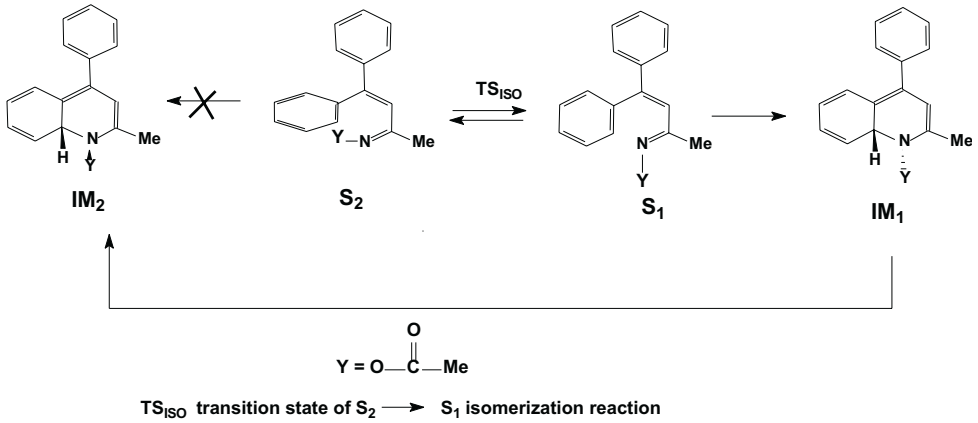


Table 4. Results of thermodynamic calculations for the hypothetical formation of 2-methyl-4-phenyl-quinoline from 4,4-diphenyl-3-buten-2-one oxime at 460 K.

Stationary structure	method	ΔH_f^o [kcal/mol]	ΔH_f *) [kcal/mol]	Entropy [cal/mol K]	ΔG or $\Delta G^{\#}$ [kcal/mol]	$T\Delta S$ or $T\Delta S^{\#}$ [kcal/mol]**)	ΔG or $\Delta G^{\#}$ [kcal/mol]**)
	MNDO	67.140	–	164.3813	–8.475	–	–
S_1	AM1	76.783	–	164.8461	0.954	–	–
	PM3	81.942	–	165.2950	5.906	–	–
	MNDO	101.033	33.893	148.2621	32.832	–7.415	41.307
TS_C	AM1	113.298	36.515	154.3264	42.308	–4.840	41.354
	PM3	109.062	27.120	151.4604	39.390	–6.364	33.484
	MNDO	80.743	13.603	155.3173	9.297	–4.169	17.772
IM_1	AM1	94.358	17.575	155.9958	22.600	–4.071	21.646
	PM3	87.818	5.876	165.9800	11.467	0.317	5.561
	MNDO	88.901	21.761	152.4888	18.756	–5.471	27.231
TS_I	AM1	101.401	24.618	153.1191	30.966	–5.394	30.012
	PM3	93.741	11.799	160.1029	20.094	–2.388	14.188
	MNDO	84.475	17.335	156.2506	12.600	–3.740	21.075
IM_2	AM1	96.127	19.344	155.8663	24.429	–4.131	23.475
	PM3	86.792	4.85	161.3572	12.677	–1.811	6.771
	MNDO	151.411	84.271	153.1183	80.977	–5.181	89.452
TS_E	AM1	145.581	68.798	152.0889	75.620	–5.868	74.666
	PM3	114.115	32.173	151.0368	44.638	–6.559	38.732
	MNDO	12.697	–54.443	161.5389	–128.751	–1.308	–120.276
P	AM1	23.498	–53.285	170.1720	–131.564	2.450	–132.518
	PM3	20.523	–61.419	172.3474	–140.699	3.244	–146.605

*) the difference between ΔH_f^o of TS, IM or P and that of S_1.
**) the difference between ΔG of TS, IM or P and that of S_1.

Orders of the bond connecting nitrogen atom with its substituent, calculated for the transition states (**TS_C**) of 4,4-diphenyl-3-buten-2-one oxime and oxime acetate electrocyclization, are close to 1, in spite of differences in the *N*-substituent (Figure 2). Therefore, according to these results, the ring closure and break of N–O bond are independent, consecutive reactions, as we postulate here.

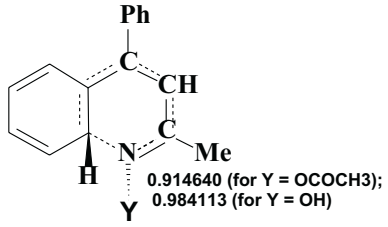


Figure 2. Calculated N–Y bond orders in **TS_C** (PM3 method).

The first two steps of the analyzed reaction are reversible endoergic processes. Therefore, the success of the whole synthesis depends to a great extent on the rate of the irreversible elimination step. If the elimination is fast, then the quinoline system is formed. In general, a mechanism of H-Y elimination from the cyclic intermediates (**IM_1** or **IM_2**, Scheme 2) is not known. In **IM_2**, obtained from the oxime acetate, the imine nitrogen atom bears a group able to leave the system together with the hydrogen atom at elevated temperatures *via* a six-membered *quasi*-aromatic transition state (E_i mechanism [22]). The thermal elimination of water from **IM_2,** possibly forming from the oxime, cannot occur *via* a six-membered transition state, but *via* much more energetic four-membered one only. This explains well why the thermal formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-3-buten-2-one oxime requires much higher temperatures and is accompanied by other reactions.

The presented results allow us to assume that also several other syntheses, which lead to heteroaromatic systems, follow mechanisms similar to that proposed here for the thermal formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-3-buten-2-one oxime acetate. One of them can be the synthesis of 2,4-diphenylquinazoline, recently announced by us [23]. After finishing our calculations, an interesting radical mechanism of the quinoxaline system from α-arylaminooximes of α-dicarbonyl compounds in acetic anhydride was proposed, basing on structures of the products only [24]. The latter reaction, in principles resembles the studied formation of the quinoline system. Therefore, some preliminary calculations assuming a homolytic N–O bond cleavage in the starting oxime acetate **S_1**, as the first step of the process, have been performed, for a comparison with the results presented here earlier. The calculations were carried out by PM3 method including HOMO-LUMO (C.I. = 2) configuration interaction [25]. According to the results obtained, this homolytic break of the N–O bond requires an energy over 42 kcal/mol, thus, more than the pericyclic reaction. Nevertheless, we will be carrying out calculations, assuming a radical process of the quinoline formation and present the results soon.

CONCLUSIONS

A choice of semiempirical method of calculations for analysis of multi-step reactions, involving stationary structures having different chemical character, requires a comparison of the obtained results with experimental kinetic data. In the case of the analyzed here thermal formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-3-buten-2-one oxime acetate, the PM3 method led to better results than MNDO and AM1 methods. According to PM3 results, the analyzed reaction consists of three thermal steps, the first (namely disrotatory electrocyclization of the starting oxime acetate) being the rate determining one.

REFERENCES

1. Jones G., *Pyridines and their Benzo Derivatives*, in *Comprehensive Heterocyclic Chemistry* Vol. 2, eds. Katritzky A.R. and Rees C.W., Pergamon Press, Oxford, 401, 1984.
2. Woodward R.B. and Hoffmann R., *The Conservation of Orbital Symmetry*, Academic Press, NY, 1970.
3. Beilstein Chemie Daten und Software GmbH and MDL Information Systems Gmbh, Beilstein Current database BS 0003AB.
4. Troszkiewicz C. and Glinka J., *Roczn. Chem.*, **36**, 1387 (1962).
5. Troszkiewicz C. and Goszczyński S., *ibid*., **37**, 919 (1963).
6. Goszczyński S., *Zeszyt. Nauk. Politechn. Sl., Chem.,* **25**, 1 (1964) in Polish, long abstract in English see *C.A*. **63**, 4253 (1965).
7. Goszczyński S. and Kucharenko A.I., *Zh. Org. Khim*., **8**, 2586 (1977).
8. Suwiński J., *Zeszyt. Nauk. Politechn. Sl.,Chem.,* **82**, 1 (1977).
9. Stewart J.J.P., *MOPAC 2000.00 Manual*, Fujitsu Limited, Tokyo, Japan (1999).
10. *Win Mopac 2.0, User Manual*, Fujitsu Limited, Tokyo, Japan (1997–98).
11. Dewar M.J.S. and Thiel W., *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977).
12. Dewar M.J.S., Zoebisch E.G., Healy E.F. and Stewart J.J.P., *J. Am. Chem. Soc*., **107,** 3902 (1985); Dewar M.J.S. and Dieter K.M., *ibid.,* **108**, 8075 (1986).
13. Stewart J.J.P., *J. Comp. Chem.*, **10**, 209, 221 (1989); **12**, 320 (1991).
14. Eigenvector Following routine: see Baker J., *J. Comp. Chem.,* **7**, 385 (1986).
15. Option existing in EF routine: see ref. [14].
16. Dewar M.J.S., Healy E.F. and Stewart J.J.P., *J. Chem. Soc. Farad. Trans. II*, **80**, 227 (1984).
17. Bartels R.H., *Report CNA-44*, 1972; see ref. [9].
18. Gordon M., modified Intrinsic Reaction Coordinate calculations, incorporated in MOPAC 2000.
19. Hirano T., see ref. [9], p. 259.
20. Minkin W., Simkin B.Ja. and Minjaev R.M., *Kwantowaja chimija organiczeskich seoedinenij, miechanizmy reakcij,* Chimija, Moskwa, 1986 p. 52-56
21. Saunders Jr W.H. and Cockeril A.F., *Mechanisms of Elimination Reactions*, John Wiley&Sons, NY, 1973, p. 390–417.
22. DePuy C.H. and King R.W., *Chem. Rev.*, **60**, 431 (1960).
23. Szczepankiewicz W., Suwiński J. and Słowikowska J., *Acta Cryst. Sect. C*, **55**, 2156 (1999).
24. Xekoukoulotakis N.P., Hadjiantoniou-Maroulis C.P. and Maroulis A.J., *Tetrahedron Letters,* **41**, 10299 (2000).
25. Multi-electron Configuration Interaction, see ref. [9] p. 176.