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Experimental and Theoretical Studies on Pyrolysis of *O*-Acetyl Derivatives of β-Phenylcinnamaldehyde and Benzaldehyde Oximes

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Thermal behavior of β-phenylcinnamaldehyde and benzaldehyde oxime O-acetyl derivatives was studied experimentally and theoretically by the semi-empirical PM3 method. Intramolecular pericyclic mechanisms were proposed for the reactions of the *E*-isomers, intramolecular catalytic polar mechanism for elimination of acetic acid from the *Z*-isomers.

Key words: aldoxime-O-acetates, cyclization, elimination, PM3 calculations

Tandem reactions belong to very useful practical methods of different systems formation. Bunce [1] and Padwa [2] described several examples of such syntheses in recent reviews. Surprisingly, these reviews do not bring examples of pericyclic tandem reactions involving thermal electrocyclization of azatrienes followed by elimination or other thermal processes and leading to aromatic systems. This type of reactions has already found numerous applications in formation of azines from acyclic systems what has been presented in our recent paper [3].

Several years ago Troszkiewicz and Glinka announced formation of 4-phenylquinoline **1** and β-phenylcinnamonitrile **2** by heating β-phenylcinnamaldoximes **3** in acetic anhydride [4]. Later Glinka showed that the quinoline and the nitrile was formed in low yields from both oxime isomers **3a** and **3b** [5]. No mechanism was formulated and no explanation for the phenomenon observed was given.

Recently we have presented some results of theoretical semi-empirical calculations concerning formation of 2-methyl-4-phenylquinoline from β-phenylbenzylideneacetone oxime *O*-acetates [6]. Comparing results of the calculations with known experimental data [7] we have concluded [6] that the reaction analyzed as well as other similar syntheses probably occur as tandem pericyclic processes involving at least two steps: thermal disrotatory electrocyclization and E_i elimination of acetic acid from cyclic intermediates. Polar and radical mechanisms were discussed too. Both oxime stereoisomers ought to form radicals with similar rates, or less stable isomer should undergo homolytic dissociation faster. In the case of β-phenylbenzylide-

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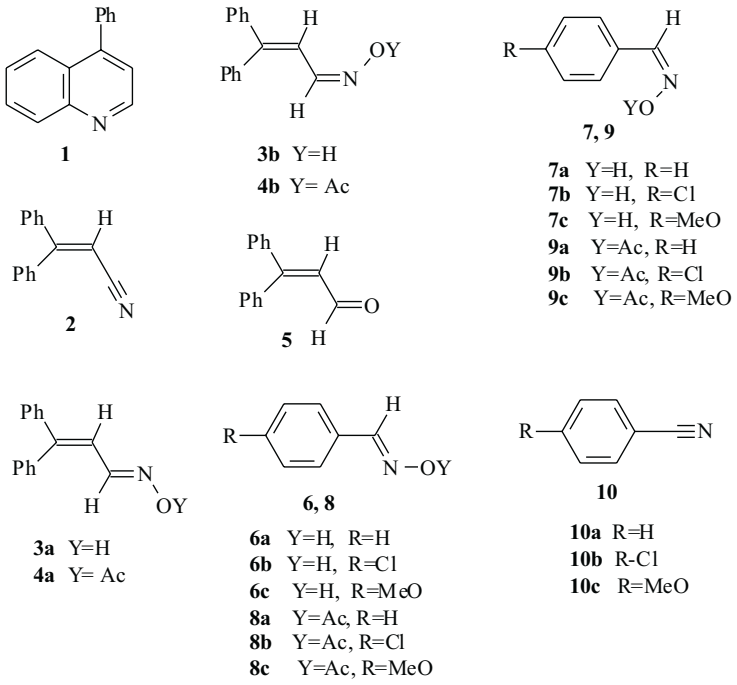


Figure 1. Structures and numbers of the compounds studied.

neacetone oxime *O*-acetates cyclization rates of the quinoline formation depend on configuration of starting isomer [6,7]. Cyclization of the less stable *Z*-isomer is preceded by its isomerization to *E*-configuration. Therefore, it is not a radical process. The same concerns thermal elimination of aldoxime *O*-acetates like **4a**, **4b**, **8a–c** and **9a–c**. The formation of nitriles by pyrolysis of *O*-substituted aldoxime derivatives has been known for a long time. *O*-Acyl benzaldoxime derivatives when heated alone or in aprotic solvents decompose almost quantitatively to nitriles and to corresponding acids [8,9]. Brady *et al.* [10,11] investigated the kinetics of pyrolysis of a number of *O*-acyl benzaldoximes and suggested that the most likely mechanism for the pyrolysis of *E*-isomers involved electron shifts inside the molecules. A polar bimolecular mechanism was proposed for the decomposition of *Z*-isomers. It is worth mentioning that these mechanisms were postulated before formulation of the Woodward-Hoffmann rules [12].

Aiming to support the pericyclic mechanism proposed by us earlier [3,6], we now present results of experimental and theoretical studies on pyrolysis of oxime *O*-acetyl derivatives of β-phenylcinnamaldehyde (**4a,b**) and benzaldehyde (**8a–c** and **9a–c**).

EXPERIMENTAL

Melting points (not corrected) were determined on Boetius HMK apparatus. EI-MS 70 eV spectra were recorded on Shimadzu GCMS QP-2000 apparatus. ^{1}H-NMR spectra were taken by Varian XL-300

spectrometer in solvents as indicated with TMS as an internal standard. UV spectra were recorded by Shimadzu UV-2102 PC recording spectrophotometer in solvents as indicated and using kuvetes 1 cm length.

Materials preparation: β-Phenylcinnamaldehyde **5**, its oximes **3a–b** and their *O*-acetates **4a–b** were prepared and purified as reported by Glinka [5]. From oximes **6a–c** and **7a–c** respective *O*-acetyl-(*E*)-benzaldoximes **8a–c** as well as *O*-acetyl-(*Z*)-benzaldoximes **9a–c** were prepared by the method described by Hauser *et al*. [13]. Solids were separated by filtration and recrystallized from proper solvents, except for the oily **8a**, which was separated by extraction with diethyl ether. Evaporation of the solvent afforded oil, which solidified on cooling below 10°C. The obtained compounds were characterized by standard methods; properties found were in accordance with the literature data; some lacking data are given below. Purity of the compounds was checked on TLC Kiselgel 60 F_{254} (Merck) plates using suitable solvents and UV-VIS (λ = 254, 366 nm) CAMAG lamp for spots detection.

5: pale yellow needles, m.p.: 44–45°C (Ref. [5] 44–44.5 °C), ^{1}H-NMR (δ, $CDCl_3$): 7.78 (1H, d, 10.2 Hz, CHO), 7.48–7.20 (10H, m, 2×C_6H_5), 6.76 (1H, d, 10.2 Hz, =CH); m/z: 208 (100, M^+), 178 (50), 131 (11), 102 (35), 77 (22), 51 (28). **3a**: pale yellow cubes, m.p.: 98–100°C (Ref. [5] 100–100.5°C), ^{1}H-NMR (δ, DMSO-d_6): 11.22 (1H, s, NOH), 7.52 (1H, d, 10.2 Hz, CH=N), 7.17–7.48 (10H, m, 2×C_6H_5), 6.82 (1H, d, 10.2 Hz, =CH); (δ, $CDCl_3$): 8.6 (1H, broad s, NOH), 7.82 (1H, d, 10.5 Hz), 7.41–7.19 (m, 10H, 2×C_6H_5), 6.78 (1H, d, 10.5 Hz, =CH). **4a**: brown needles, m.p.: 108–110°C (Ref. [5] 109–110°C), ^{1}H-NMR (δ, DMSO-d_6): 7.50 (1H, d. 10.2 Hz, CH=N), 7.54–7.17 (m, 2× C_6H_5), 6.82 (1H, d, 10.2 Hz, =CH), 1.66 (3H, s, CH_3). **3b**: yellow needles, m.p.: 129–131°C (Ref. [5] 132.5–133°C), ^{1}H-NMR (δ, DMSO-d_6): 11.40 (s, 1H, NOH), 7.45–7.20 (11H, m, CHN + 2×C_6H_5). **4b**: bright brown needles, m.p.: 85–86°C (Ref. [5] 86–88°C), ^{1}H-NMR (δ, DMSO-d_6): 7.53–7.18 (10H, m, 2×C_6H_5), 7.44 (1H, d, 9.3 Hz, CHN) 6.92 (1H, d, 9.3 Hz, =CH), 1.66 (3H, s, CH_3). **6a:** colorless prisms, m.p.: 34–36°C (Ref. [14] 34–36°C), ^{1}H-NMR (δ, $CDCl_3$): 8.46 (1H, s, NOH); 8.09 (1H, s, CHN); 7.53–7.49 (2H, m, CH-arom.); 7.33–7.31 (3H, m, CH-arom.). **8a**: colorless oil m.p.: 14–15°C, b.p.: 138–140°C/14 mmHg (Ref. [15] b.p.: 123°C/4 mmHg, m.p.: 14–16°C), ^{1}H-NMR (δ, $CDCl_3$): 8.34 (1H, s, CHN); 7.73–7.70 (2H, m, CH-arom.); 7.43–7.34 (3H, m, CH-arom.); 2.21 (3H, s, CH_3). UV: λ_{max} = 255.2 nm, $\varepsilon = 1.95\times 10^4$ L mol^{-1} cm^{-1}. **7a**: colorless needles, m.p.: 128–130°C (Ref. [16] 129–131°C), ^{1}H-NMR (δ, $CDCl_3$): 8.76 (1H, s, CHN); 7.97–7.92 (2H, m, CH-arom.); 7.48–7.40 (4H, m, CH-arom. + CHN). **9a**: colorless needles, m.p.: 56–58°C (Ref. [17] 55–56°C), ^{1}H-NMR (δ, $CDCl_3$): 7.87–7.84 (2H, m, CH-arom.); 7.72 (1H, s, CHN); 7.51–7.48 (3H, m, CH-arom.); 2.29 (3H, s, CH_3); UV: λ_{max} = 247.2 nm, $\varepsilon = 1.92\times 10^4$ $Lmol^{-1}$ cm^{-1}. **6b:** colorless needles, m.p.: 108–110°C (Ref. [18] 110–111°C), ^{1}H-NMR (δ, $CDCl_3$): 8.11 (1H, s, NOH); 7.83 (1H, s, CHN); 7.53–7.50 (2H, m, CH-arom.); 7.38–7.34 (2H, m, CH-arom.). **8b:** pale yellow needles, m.p.: 69–70°C (Ref. [19] 67°C), ^{1}H-NMR (δ, $CDCl_3$): 8.33 (s, 1H, CHN); 7.70–7.67 (2H, d, 8.4 Hz CH-arom.); 7.43–7.40 (2H, d, 8.4 Hz, CH-arom.); 2.24 (3H, s, CH_3); UV: λ_{max} = 261.4 nm, $\varepsilon = 2.4\times 10^4$ $Lmol^{-1}$ cm^{-1}. **7b:** colorless needles, m.p.: 141–143°C (Ref. [20] 142°C), ^{1}H-NMR (δ, $CDCl_3$): 8.77 (1H, broad s, NOH); 7.91–7.88 (2H, m, CH-arom.), 7.42–7.35 (3H, m, CH-arom. + CHN). **9b:** colorless crystals, m.p.: 90–91°C (Ref. [21] 86–87°C), ^{1}H-NMR (δ, $CDCl_3$): 7.81 (2H, d, 8.4 Hz, CH-arom.); 7.68 (1H, s, CHN); 7.02 (2H, d, 8.4 Hz, CH-arom.); 2.29 (3H, s, CH_3); UV: λ_{max} = 256.2 nm, $\varepsilon = 2.29\times 10^4$ $Lmol^{-1}$ cm^{-1}. **6c:** pale yellow crystals, m.p.: 64–66°C (Ref. [22] 64°C), ^{1}H-NMR (δ, $CDCl_3$): 8.73 (1H, broad s, NOH); 7.97 (1H, s, CHN); 7.64 (2H, d, 8.4 Hz, CH-arom); 6.94 (2H, d, 8.4 Hz, CH-arom.); 3.83 (3H, s, OCH_3); **8c:** pale yellow crystals, m.p.: 46–48°C (Ref. [23] 48–49°C), ^{1}H-NMR (δ, $CDCl_3$): 8.29 (1H, s, CHN); 7.68 (2H, d, 8.7 Hz, CH-arom.); 6.94 (2H, d, 8.7 Hz, CH-arom.); 3.85 (3H, s, OCH_3); 2.22 (3H, s, CH_3); UV: λ_{max} = 276.2 nm, $\varepsilon = 2.44\times 10^4$ $Lmol^{-1}$ cm^{-1}. **7c:** colorless prisms, m.p.: 129–131°C (Ref. [24] 131–132°C), ^{1}H-NMR (δ, $CDCl_3$): 9.13 (1H, broad s; NOH); 7.52 (2H, d, 8.7 Hz, CH-arom.); 6.94 (2H, d, 8.7 Hz CH-arom); 3.85 (3H, s, OCH_3); **9c:** colorless crystals, m.p.: 64–66°C (Ref. [25] 64–65°C), ^{1}H-NMR (δ, $CDCl_3$): 8.29 (1H, s, CHN); 7.68 (2H, d, 8.4 Hz, CH-arom.); 6.92 (2H, d, 8.4 Hz, CH-arom.); 3.85 (3H, s, OCH_3); 2.22 (3H, s, CH_3); UV: λ_{max} = 271.6 nm, $\varepsilon = 2.24\times 10^4$ $Lmol^{-1}$ cm^{-1}.

Thermal reactions of β-phenylcinnamaldoximes (3) and its *O*-acetates (4). General procedure: **4a** or **4b** (0.27 mmol) was added to a boiling solvent: decalin (10 ml) or acetic anhydride (10 ml), then refluxed for 6 hrs. In other experiments **3a** or **3b** was heated under reflux in a mixture of decalin (10 ml) and acetic anhydride (0.2 ml). The resulting solutions were cooled down, acidified with hydrochloric acid (5%, 10 ml) and distilled with water. The distillates from acidic solution were collected, diluted with methanol to volumes suitable for UV analysis and photometred. Yields of **2** were calculated from readings

at 284.4 nm. The residual acidic solutions in the distillation flask were alkalized with aqueous sodium hydroxide (20%, 24 ml) and again distilled with water. The second distillates were collected, diluted with water and UV photometred. Yields of **1** were calculated from readings at 315 nm. In some experiments with decalin as a solvent phenolic radical scavengers (α-naphtol or Topanol-O, 0.1 g) were added before heating.

Macrokinetic measurements of nitrile formation: General procedures. Method A: To a boiling solvent (20 ml) [decalin 465 K, n-octane 400 K, n-heptane 369 K or cyclohexane 353 K] **8a–c** or **9a–c** (50 mg, ~0.3 mmol) was added in one portion. Samples (0.2 ml) were taken from the reaction mixture at certain time intervals, each sample was transferred into a 25 ml measuring flask and quickly diluted with cold methanol to 25 ml volume and then its UV-spectrum was recorded. The reaction was prolonged until two following samples showed very similar absorbencies, and then the kinetic curves were plotted. Two examples of the measurements are shown below (Fig. 2 and 3).

Values of rate constants for the thermal elimination of *Z*-isomers (**9a–c**) were usually less accurate than those of *E*-isomers (**8a–c**) and the second order kinetics was followed only to circa 80–90% conversion of the starting material.

Method B: A similar procedure to A, with a pre-added equivalent amount of acetic acid (0.018 g, 0.3 mmol) to the reaction mixture before the addition of the oxime derivative.

Method C: A similar procedure A, with the addition of an equivalent amount of the radical scavenger Topanol-O (0.06 g, 0.3 mmol) to the reaction mixture 15 minutes following the addition of the oxime derivative.

Method D: A similar procedure to A, starting with double amount of the oxime derivative (100 mg) in the same volume of a solvent (20 ml). Samples (0.2 ml) were diluted with methanol up to 50 ml before UV-spectrum reading.

Time (min)	Abs. (subs.)	$\log \frac{A_\infty - A_0}{A_\infty - A_t}$	$k \times 10^5$ (s^{-1})	1st order kinetic curve
0	2.393 A_0	–	–	
5	2.366	0.00520	3.98	
10	2.336	0.01100	4.23	
15	2.307	0.01680	4.29	
30	2.222	0.03400	4.36	
60	2.056	0.06990	4.47	
120	1.780	0.13680	4.37	
180	1.550	0.20180	4.30	
240	1.320	0.27830	4.45	
	0.125 A_∞ yield = 95%			
Average value of k = (4.30±0.15) × 10^{-5} (s^{-1})				

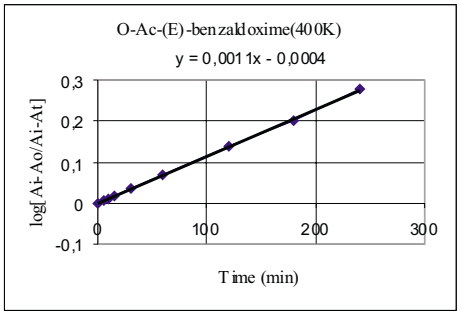


Figure 2. Thermal elimination of **8a** in octane (400 K) method A.

Macrokinetics of thermal reactions of β-phenylcinnamaldoxime *O*-acetates (4a–b): To a boiling decalin (465 K, 20 ml) **4a** or **4b** (50 mg, ~0.188 mmol) was added at once. Samples (0.2 ml) were taken from the reaction mixture at certain time intervals, each sample was transferred into a 25 ml measuring flask and quickly diluted with cold methanol to 25 ml volume and then its UV-spectrum was recorded. The reaction was prolonged until two following samples at 284.5 nm showed very similar absorbencies, and then the kinetic curves were plotted. Values of 1st order rate constant ($k = 3.2 \times 10^{-4}\ s^{-1}$) for the thermal elimination of *E*-isomer **4a** were not accurate, due to parallel formation of **1** and **2**. It also concerns rate constant of fast 2nd order reaction of *Z*-isomer **4b** ($k = 8.1 \times 10^{-2}\ M^{-1}\ s^{-1}$) though it undergoes elimination only.

Time (min)	λ	$\lambda-\lambda_0/\lambda_\infty-\lambda$	$\{1/[A_0]\}\times\{\lambda-\lambda_0/\lambda_\infty-\lambda$	$k\times10^2$ ($M^{-1}\,s^{-1}$)	2st order kinetic curve
0	2.364	–	–	–	
5	2.142	0.1097	7.1551	2.38	
10	1.952	0.2247	14.6552	2.44	
15	1.780	0.3516	22.9246	2.54	
30	1.475	0.6556	42.7466	2.37	
60	1.100	1.2885	84.0112	2.33	
90	0.891	1.9080	124.407	2.30	
120	0.759	2.5078	163.514	2.27	
150	0.654	3.1962	208.402	2.31	
∞	0.119				
($k = 2.37\pm0.20\times10^{-2}\ M^{-1}\,s^{-1}$) M = mol/L					

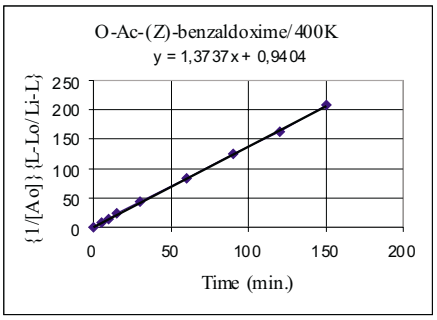


Figure 3. Thermal elimination of **9a** in octane (400 K), method A.

Thermal elimination of 6a in the presence of acetic anhydride: Procedure: **6a** (0.05 g, 0.41 mmol) and acetic anhydride (0.083 g, 0.82 mmol) in n-octane (20 ml) was kept at room temperature for 5 min, then was quickly heated up till reaching the boiling point of octane (127°C) and was worked up as described in a general procedure. An example is given in Fig. 4.

Time (min)	Abs. (subs.)	$\log\frac{A_\infty - A_0}{A_\infty - A_t}$	$k\times10^5$ (s^{-1})	1st order kinetic curve
0	2.393 A_0	–	–	
10	2.339	0.01046	4.02	
15	2.308	0.01659	4.25	
30	2.222	0.03400	4.36	
60	2.056	0.06990	4.47	
120	1.780	0.13680	4.37	
180	1.540	0.20488	4.37	
240	1.320	0.27830	4.45	
	0.125 A_∞ yield = 95%			
Average value of $k = (4.32\pm0.15)\times10^{-5}$ (s^{-1})				

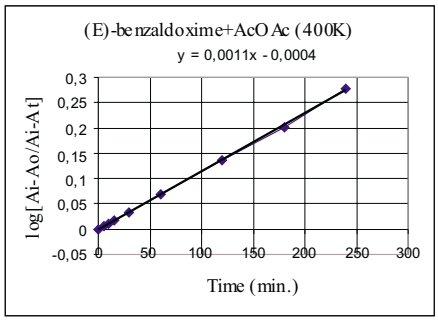


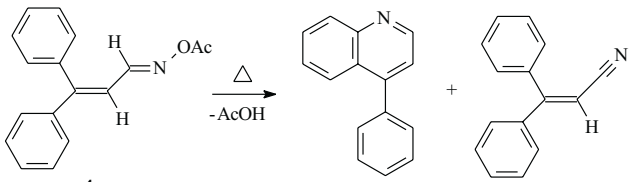
Figure 4. Thermal elimination of **6a** in n-octane/Ac_2O (400 K).

Calculation procedures: The calculations were performed by PM3 method on PC computers (Pentium III, 733 MHz) using MOPAC 2000 program package [26] with WinMopac 2.0 [27] as a graphic interface. Structures of starting materials S (oxime acetates **4a–b**, **8a–c** or **9a–c**) as well the expected products P (**1**, **2, 10a–c** + acetic acid) were optimized by EF procedure. The energetic profile of the electrocyclization of **4a–b** and Ei eliminations of **4a, 8a–c** and IMc(S2) were studied by reaction-path (also using EF procedure) and by saddle methods, inversion on nitrogen atom in intermediate IMc(S1) by saddle only; these finished in obtaining of local maxima close to transition states TS of each step. The transition states were found by NLLSQ and TS procedures, followed by IRC = ± 1 calculations. All stationary structures were optimized to gradients less than 0.01. Then *THERMO* calculations were performed. Other details concerning the methods of calculations were given earlier [3]. In some cases, indicated later, electron configuration interactions (C.I. = 2) were involved into the calculations.

RESULTS AND DISCUSSION

Thermal reactions of β-phenylcinnamaldoxime *O*-acetates (4a–b): Mixtures of stereoisomeric **3** or their *O*-acetates **4** when heated in decalin with acetic anhydride or in acetic anhydride itself always afforded mixtures of 4-phenylquinoline (**1**, Pc) and β-phenylcinnamonitrile (**2**, PE) (Scheme 1). Also **4a** (S1) when heated in decalin or in boiling acetic anhydride gave a mixture of easily separated **1** (Pc) and **2** (PE) in proportion close to 1:5.4. Overall yields of the products were over 90% of theoretical. In contrast to that heating of **4b** (S2) afforded exclusively **2** (PE). No absorption of **1** could be detected. The presence of phenolic radical scavengers in the reaction media has affected neither structures nor yields of the products.

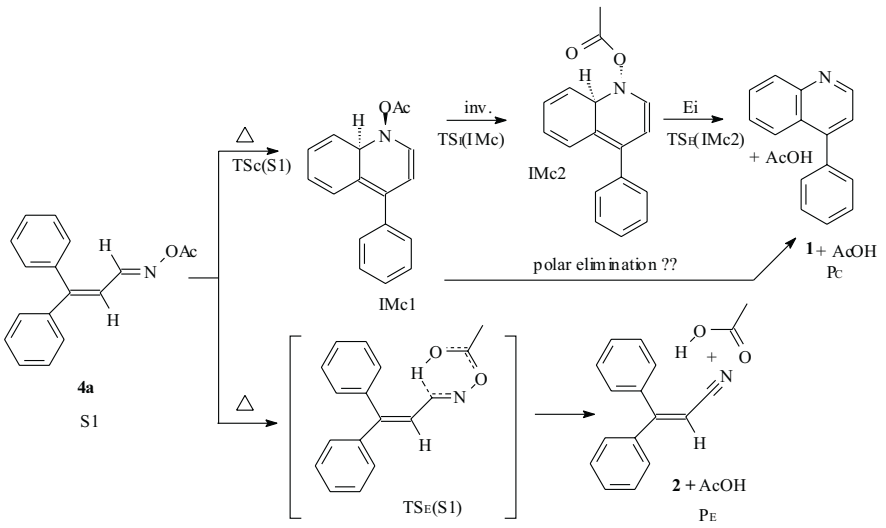
Scheme 1



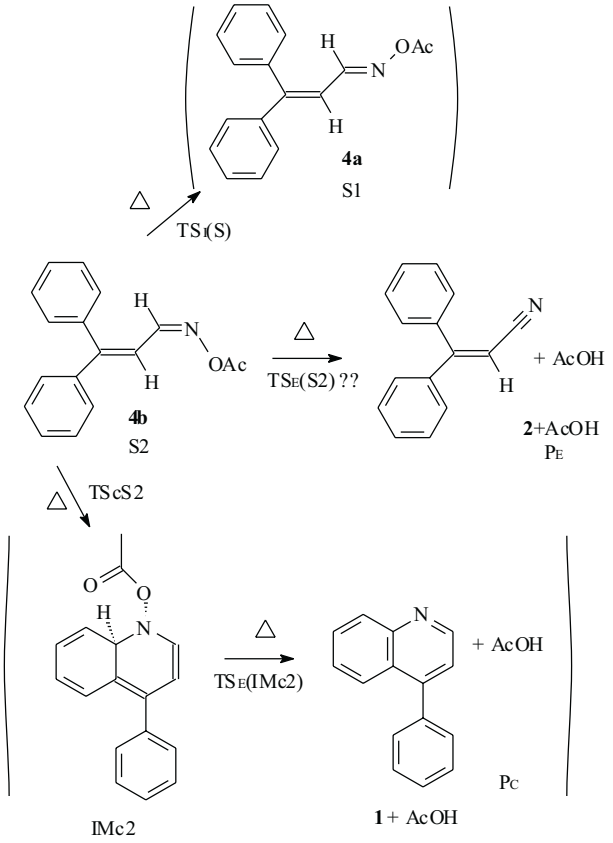
4a (S1) **1** (Pc) **2** (PE)

Trying to explain the experimentally observed results (parallel formation of **1** (Pc) and **2** (PE) from **4a** (S1) and formation of **2** (PE) from **4b** (S2)), Schemes 2 and 3 we performed respective calculations assuming thermal pericyclic mechanisms for the products formation. Particularly interesting were the differences in thermal behavior of (*Z*)-*O*-acetates of β-phenylbenzylideneacetone oxime [6,7] and of **4b** (S2). The former one afforded the respective quinoline derivative following *Z*→*E*-isomerization. The later one underwent exclusively elimination.

Scheme 2



Scheme 3



More important results of our calculations on thermal behavior of **4a–b** (S1 and S2) assuming pericyclic mechanism and additionally some data for radical decomposition of **4a** are collected in Table 1.

Data concerning activation free enthalpies of possible thermal Beckmann rearrangements of **4a–b**, calculated for 460 K in vacuum, are as follows: for **4a** (S1): $\Delta\Delta G^{\#}$ over 335 kJ/mol; for **4b** (S2): $\Delta\Delta G^{\#}$ over 270 kJ/mol. These values exceed much values of free enthalpies of activation (Table 1) for the reactions shown in Schemes 1–3 and considered here. Calculated activation free enthalpy for the homolytic break of N–O bond in **4a** (S1) at 460 K TSdh(S1) is close to 210 kJ/mol. A very similar activation free enthalpy was found for the homolytic decomposition of **4b** (S2). These values are also higher than those for TSc(S1) and TSE(S1) though lower than one for TSc(S2) and very close to that for TSi(S). Unfortunately we were not able to calculate either TSE(S2) or TSE(IMc1), in which the eliminated parts of acetic acids are in positions not suitable for a concerted reaction.

Table 1. PM3 calculation results concerning thermal behavior of β-phenylcinammaldehyde oxime-*O*-acetates assuming pericyclic or radical mechanisms of reactions.

Structure symbol	ΔH_f [J/mol] and ΔS [J/mol K] at 460 K	ΔG or $\Delta G^{\#}$ [kJ/mol] at 460 K	$\Delta\Delta G$ or $\Delta\Delta G^{\#}$ [kJ/mol] at 460 K *)
4a, S1	209930 791.3	 –156.5	– –
4a, S1**) C.I. = 2	206300 788.9	 –156.5	 0.00
TSdh(S1)**) C.I. = 2	399555 755.8	 +51.9	 +208.4
4b, S2	208100 307.0	 –154.1	 2.4
4b, S2**) C.I.= 2	207188 786.3	 –154.5	 2.1
TSiS	374677 728.5	 +165.8	 +194.6$^{\#}$
TSc(S1)	343929 731.7	 +7.4	 +163.9$^{\#}$
TSc(S2)	422806 729.0	 +87.4	 +244.0$^{\#}$
IMc1	237392 740.0	 –103.0	 +53.5
IMc2	244647 754691	 –102.5	 +54.1
TSi(IMc)	269578 735.8	 –68.9	 +87.7$^{\#}$
TSE(S1)	348769 780.3	 –10.2	 +146.4$^{\#}$
TSE(S2)	?	?	Not calculated
TSE(IMc1)	?	?	Not calculated
TSE(IMc2)	271895 717.3	 –58.1	 +98.5$^{\#}$
1 +AcOH, Pc	–82049 753.8	 –428.9	 –272.3
2 +ACOH, PE	35437 714.2	 –293.1	– –136.5

*) All $\Delta\Delta G$ and $\Delta\Delta G^{\#}$ values were calculated in respect to ΔG of S1.
**) Calculations involving electron configuration interactions.

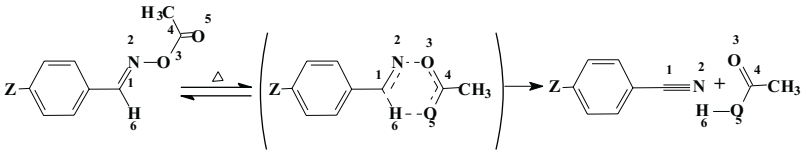
Comparing the calculated data of $\Delta\Delta G$ and $\Delta\Delta G^{\#}$ for the reactions shown in Schemes 2 and 3 one can draw the following conclusions. Both reactions: elimination and formation of **1** from **4a** (S1) are practically irreversible leading to the very stable products, the cyclization being thermodynamically favored. In vacuum at 460 K the elimination of **4a** (S1) to **2** (PE) by a concerted reaction is faster than cyclization of **4a** (S1) to **1** (Pc). The formation of **1** (Pc) from **4a** (S1) is probably three-step tandem pericyclic process involving reversible disrotatory electrocyclization of **4a** (S1) to IMc(S1), isomerization of IMc(S1) to IMc(S2) and a concerted elimination of acetic acid from IMc(S2) to afford **1** (Pc). Thermal isomerization of **4a** (S1) to **4b** (S2) and the reverse are slow processes. Thermal electrocyclization of **4b** (S2) is highly un-

favorable due to its very high activation free enthalpy. As the mechanism of thermal elimination of *Z*-aldoxime-*O*-acetates is not known we were not able to calculate ΔG of TSE(S2).

Assuming that *β*-phenylcinnamaldehyde and benzaldehyde oxime-*O*-acetates should thermally eliminate acetic acid according to similar mechanisms, depending only on configuration of C=N bond, we studied thermal behavior of readily available derivatives of benzaldoximes.

Thermal elimination of *O*-acetyl-(*E*)-benzaldoximes (8a–c): The pyrolysis of **8a–c** (S3) were studied experimentally and theoretically, and it is believed that the pyrolysis proceeds *via* a typical retro-ene mechanism with a six-membered transition state (Scheme 4).

Scheme 4



8a-c **10a-c** + AcOH

S3 **TSE(S3)** **PE(S3)**

Thus, the study was extended first to the thermal elimination of *O*-acetyl-(*E*)-benzaldoxime (**8a**), then to its *p*-chloro (**8b**) and p-methoxy (**8c**) derivatives. The elimination showed the first-order kinetics, with a linear plot of $\log[(A_\infty - A_0)/(A_\infty - A_t)]$ against time up to 90% of the conversion (A_∞ is the absorbance of the starting material at infinitive reaction time, A_0 and A_t are its absorbancies at zero and t time respectively), (Table 2).

Table 2. Rate constants for the pyrolysis of **8a–c** (S3).

X No.	Method	$k\times10^6$ (s^{-1}) at 353 K	$k\times10^6$ (s^{-1}) at 369 K	$k\times10^6$ (s^{-1}) at 400 K	$k\times10^6$ (s^{-1}) at 465 K	Ea [kJ/mol]	$\log(k_X/k_H)$	σ
H	A	0.41	2.26	43.0	5060	116.7[a]	0	0
(8a)	B		–	42.9		113.5[b]		
	C		–	43.4		(114.72)[c]		
	D		–	42.9				
Cl	A	very	1.65	31.8	4440	117.2[a]	–0.13	+0.227
(8b)		slow				117.6[b]		
						(117.5)[c]		
MeO	A	0.525	2.75	46.2	5120	111.8[a]	+0.09	–0.268
(8c)						112.1[b]		
						(112.0)[c]		

[a]) E_a calculated between 369 K to 400 K.
[b]) E_a calculated between 400 K to 465 K. [c]) Ea calculated from the kinetic plot.

The rate of pyrolysis was not affected either by change of the starting material concentration or by pre-added acetic acid. To check whether a free radical mechanism is participating in the overall pyrolytic process of **8a–c**, the reaction was repeated in the presence of Topanol'O' (a known free radical scavenger). The presence of Topanol'O' did not affect the rate of pyrolysis, pointing out to insignificant participation of free radical processes in the overall mechanism of the reaction. The small significance of electronic effects of substituents at the benzene ring on the rates of thermal elimination can be treated as a supporting evidence for the concerted mechanism.

Also semi-empirical calculations were performed for the thermal elimination of **8a–c**. The starting structures **8a–c** (S3) were optimized in their most stable conformer (*s-trans*). Reaction-path calculations were carried out by decreasing the distance between O^5–H^6 as illustrated in Scheme 4, these finished in obtaining of local minima close to products **10a–c** + AcOH PE(S3), (nitriles + acetic acid). The maxima on the energy profiles were optimized to give TSE(S3) structures. *IRC* and *THERMO* calculations led to the results summarized in Table 3. From the PM3 calculations we could notice that a change of *p*-substituent in the aromatic nucleus resulted in very small effects on the calculated activation free enthalpies of elimination. This result and negative values of activation entropies are, at least qualitatively, in accordance with the experimental results and with the suggested concerted mechanism.

Thermal elimination of *O*-acetyl-(*Z*)-benzaldoximes 9a–c: The pyrolysis of **9a–c** must occur according to a mechanism different from E_i characteristic for decomposition of the corresponding *E*-isomers **8a–c**. There is no chance to involve a six-membered cyclic transition state in the reaction of *Z*-isomers without their former isomerization. Brady *et al*. [10] reported that **9a** was very easily isomerized in the presence of acids. Nevertheless, a mechanism of **9a–c** elimination following their isomerization to **8a–c** can be ruled out because the rate constants of pyrolysis of **9a–c** are *ca* 10000 times faster than that of the corresponding **8a–c**.

What more, acids do not catalyze the elimination of the *E*-isomers **8a–c** (in contrast to the elimination of *Z*-isomers **9a–c**). We found that rates of **9a–c** pyrolysis were greatly affected by changes in the initial concentrations of the starting acetates. The rates also depended on the presence of a pre-added acetic acid or even on the presence of slightly acidic Topanol 'O' (used by us as a radical scavenger to check a possible participation of a free radical mechanism). Consequently we suggest that the pyrolysis of **9a–c** is a catalytic process following the second-order kinetics. Some results of macrokinetic experiments assuming the second-order elimination are summarized in Table 4. Additionally acids catalyze the reaction what complicates the kinetics particularly at higher concentrations and higher conversions of the starting material when a concentration of eliminated acetic acid should not be neglected. The probable mechanism of the elimination in aprotic solvents (without of acidic catalysis) is shown in Scheme 5.

Table 3. PM3 calculation results concerning thermal behavior of **8a–c** assuming pericyclic mechanisms of reactions.

Structure No.		N–O[a] N–C	O–H[a] C–H	370 K			400 K			460 K		
				ΔH^b ΔS^c	ΔG^d	$\Delta\Delta G^{\#d}$ or $\Delta\Delta G$	ΔH^b ΔS^c	ΔG^d	$\Delta\Delta G^{\#d}$ or $\Delta\Delta G$	ΔH^b ΔS^c	ΔG^d	$\Delta\Delta G^{\#d}$ or $\Delta\Delta G$
	S3	1.409	1.899	9052			15734			30275		
		1.296	1.115	505.1	–17.8		522.5	–25.8		556.3	–225.6	
H	TSE(S3)	1.815	1.382	129029			135468			149506		
(8a)		1.230	1.361	483.3	–49.8	128.0	500.0	–64.6	128.7	532.7	–95.5	+130.1
	PE(S3)	6.944	0.958	–178.345			–171918			–157960		
		1.160	4.293	510.9	–367.4	–349.6	527.6	–383.0	–357.2	560.1	–415.6	–190.0
	S3	1.407	1.898	–17802			–10680			4723		
		1.296	1.115	537.672	–216.8		556.176	–233.2		592.010	–267.6	–
Cl	TSE(S3)	1.809	1.373	103648			110569			125487		
(8b)		1.232	1.362	516.263	–86.6	129.4	534.151	–103.1	130.1	568.855	–134.8	132.8
	PE(S3)	6.776	0.957	–203.177			–196306			–181484		
		1.160	4.214	532.845	–400.3	183.5	550.692	–416.6	183.4	585.171	–450.5	–182.9
	S(3)	1.411	1.898	–148966			–140923			–123448		
		1.297	1.115	572.045	–360.6		592.941	–378.1		633.598	–414.9	
MeO	TSE(S3)	1.818	1.384	–29513			–21704			–4714		
(8c)		1.231	1.360	548.136	–232.3	128.3	568.417	–249.1	129.0	607.950	–284.4	130.3
	PE(S3)	7.028	0.958	–336878			–328597			–310719		
		1.160	4.334	624.376	–567.7	–207.1	645.897	–587.8	–209.7	687.495	–626.8	–211.9

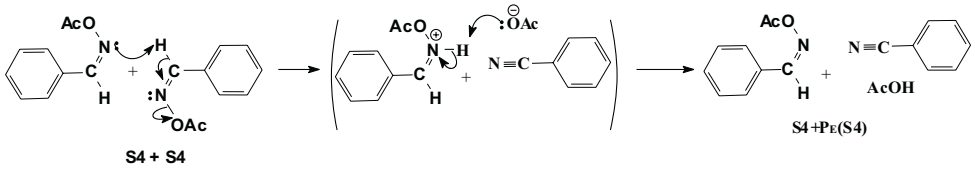
[a]) bond lengths measured in Å, [b]) measured in J/mol, [c]) measured in J/molK, [d]) measured in kJ/mol.

Table 4. Rate constants of the pyrolysis of *O*-acetyl-(*Z*)-benzaldoximes **9a–c** (S4).

X No.	Method	$k\times10^4$ [M^{-1} s^{-1}] at 353 K	$k\times10^3$ [M^{-1} s^{-1}] at 369 K	$k\times10^2$ [M^{-1} s^{-1}] at 400 K	$k\times10^6$ [M^{-1} s^{-1}] at 465 K	Ea [kJ/mol]	$\log(k_X/k_H)$	σ
H	A	5.96	2.32	2.37	very fast	92.00[a]	0	0
(9a)	B	–	66.4	–	–	92.00[b]		
	C	–	21.8	–	–	92.00[c]		
	D	–	3.1	–	–			
Cl	A	very slow	1.94	2.24	very fast	96.86[b]	–0.08	+0.227
(9b)						96.76[c]		
MeO	A	9.96	3.43	2.99	very fast	83.78[a]	+0.17	–0.268
(9c)						85.73[b]		
						84.98[c]		

[a]) E_a calculated between 335 K to 369 K, [b]) E_a calculated between 369 K to 400 K,
[c]) E_a calculated from the kinetic plot.

Scheme 5



Our attempts to simulate the reaction according to Scheme 5 (by PM3 method) have led to unexpected results. Shortening the distance between nitrogen atom of one molecule of the oxime *O*-acetate and methine hydrogen atom of the similar second molecule (from 16 to 14 Å) resulted in a slow continuous decrease in heats of formation of the system (from *ca* –37.66 to –38.07 kJ/mol at 298 K). When the distance was *ca* 14 Å, a new system was formed with a sudden drop of heat of formation to –215 kJ/mol. The new system contained three molecules: **9a** (S4), **10a** and acetic acid. All atoms in **10** and in acetic acid were from the same molecule of the starting **9a**. Further optimization of the new system resulted only in shortening of the distance between methine hydrogen and nitrile nitrogen atoms to *ca* 10 Å with slight drop of heat of formation to –225 kJ/mol.

In contrast to that simulation of a typical E2cB process shown in Scheme 6 was easy and finished in obtaining the expected result. The calculated free enthalpy of activation ($\Delta\Delta G^{\#}$) for the thermal elimination of **9a** (S4) in vacuum at 460 K in the presence of acetate anion (AcO^-) was lower than 42 kJ/mol in respect to the reagents separated, therefore, three times lower than for the concerted thermal elimination of the corresponding *E*-isomer **8a**. See data in Table 5.

Scheme 6

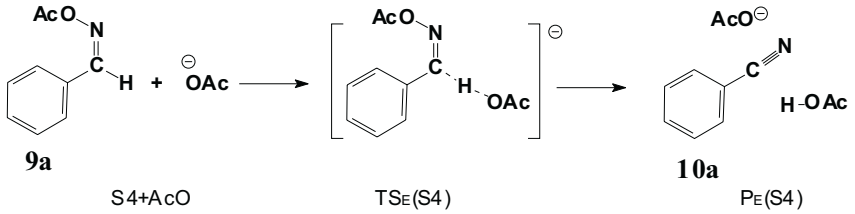


Table 5. E2cB elimination of **9a** (S4) in the presence of acetate anion; the results of PM3 calculations in vacuum at 460 K.

structure	Ac**O**....**H**C=N distance	ΔH_f [J/mol] and ΔS [J/molK] at 460 K	ΔG [kJ/mol] at 460 K	$\Delta\Delta G$ or $\Delta\Delta G^{\#}$ [kJ/mol] at 460 K
9a + AcO^- S4 + AcO	1.755 Å (minimum of ΔH_f)	–536530 742.297	–878.0	–
TSE(S4)	1.343 Å	–500762 730.270	–836.7	+41.3$^{\#}$
10a + AcO^- + AcOH PE(S4)	0.969 Å	–316342 587.476	–1005.3	–215.5

$\Delta\Delta G$ or $\Delta\Delta G^{\#}$ in respect to S4 + AcO in minimum.

Situation in the latter simulation seems to be far from real experimental conditions, though the presence of acetate anion in the reaction medium cannot be ruled out. Nevertheless, the results of calculations show that even in aprotic solvents reactions can be catalyzed by base and that this type of catalysis can drastically reduce the activation free enthalpy of elimination. In this sense the results of calculations shown in Table 5 are in agreement with experiments and with our view on the mechanism of thermal reactions of aldoxime *O*-acetates, being under consideration in this work.

The results of experiments and of the calculations do not rule out completely a possible direct elimination of acetic acid from the intermediate IMc(S1), forming as the result of disrotatory electrocyclization of **4a** (S1). Nevertheless, it seems more likely that the elimination step is preceded by inversion on the ring nitrogen atom, because this reaction requires very low free enthalpy of activation and because a rate of the second-order elimination of acetic acid from IMc(S1) would change with changes of starting material concentrations, what was not observed by us.

CONCLUSIONS

All oxime *O*-acetyl derivatives of β-phenylcinnamaldehyde **4a–b** and benzaldehyde **8a–c** and **9a–c** in aprotic solvents undergo thermal decomposition to corresponding nitriles **2**, **10a–c** and acetic acid. (*E*)-Isomers **4a** and **8a–c** react according to an intramolecular concerted pericyclic mechanism. The derivative of β-phenylcinnamalde-

hyde **4a** besides the respective nitrile **2** affords quinoline **1**. The later tandem reaction probably involves three steps: disrotatory electrocyclization, inversion on the ring nitrogen atom in the forming cyclic intermediate and a concerted elimination of acetic acid from the inverted intermediate. The electrocyclization step is a rate determining one. The pericyclic mechanisms of both reactions: elimination and cyclization were supported by respective semi-empirical PM3 calculations. In contrast to the above, intermolecular catalytic mechanism for elimination of acetic acid from the *Z*-isomers **4b**, **9a–c** is proposed.

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