Chemistry of Heterocyclic Compounds, Vol. 41, No. 10, 2005

INVESTIGATION OF THE INTERACTION OF 5-ARYL-2,3-DIHYDRO-2,3-FURANDIONES WITH COMPOUNDS CONTAINING C=N AND C≡N BONDS SIMULTANEOUSLY

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Aroylketenes, generated by the thermolysis of 5-aryl-2,3-dihydro-2,3-furandiones, react with S-methyl-N-cyano-N'-phenylisothiourea, N-cyano-N',N'-dimethylformamidine, and N,N-bis(β-cyanoethyl)-cyanamide with the formation of 6-aryl-2-[(methylthio)(phenylamino)methylene]amino-, 6-aryl-2-dimethylaminomethyleneamino-, and 6-aryl-2-[N,N-bis(β-cyanoethyl)amino]-4H-1,3-oxazin-4-ones respectively. Modeling has been carried out of the interaction of benzoylketene with the indicated cyano compounds by the SSP MO LCAO semiempirical method using the MNDO-PM3 approach. A mechanism is proposed for the formation of substituted 4H-1,3-oxazin-4-ones.

Keywords: 5-aryl-2,3-dihydro-2,3-furandiones, aroylketenes, N,N-bis(β-cyanoethyl)cyanamide, N-cyano-N',N'-dimethylformamidine, 2-substituted 6-aryl-4H-1,3-oxazin-4-ones, S-methyl-N-cyano-N'-phenylisothiourea, cyano[di(methylthio)]imidocarbonate, SSP MO LCAO semiempirical method in MNDO-PM3 approach, [4 + 2] cycloaddition.

It is known that thermolysis of 5-aryl-2,3-dihydro-2,3-furandiones (benzene, 80°C) is accompanied by the elimination of carbon monoxide and leads to 3-aroyl-6-aryl-4-hydroxy-2H-pyran-2-ones [1]. The formation of substituted pyrans in this reaction is explained by the dimerization of aroylketenes, the primary thermolysis products. The fact of forming aroylketenes as a result of thermal decarbonylation of furandiones was reliably confirmed in [2].

It was shown previously that aroylketenes generated in a similar way react with compounds containing a C=N bond and an activated C≡N bond with the formation of [4 + 2] cycloaddition products, 6-substituted 3,4-dihydro-2H-1,3-oxazin-4-ones [3-5] or 4H-1,3-oxazin-4-ones [6-8] respectively. Many of the 1,3-oxazines obtained in this way display biological activity [9], which makes it expedient to study these reactions further.

In the presence of compounds with an unactivated cyano group (MeCN, PhCN) aroylketenes are dimerized [7].

The interaction of 5-aryl-2,3-dihydro-2,3-furandiones with compounds containing C=N and C≡N bonds simultaneously, and also activated and unactivated C≡N bonds is practically unstudied. It is known only that as a result of the reaction of 5-aryl-2,3-dihydro-2,3-furandiones with methylenaminoacetonitrile, a compound containing isolated C=N and C≡N bonds (toluene, 110°C, 1.5 h), the latter reacts as an azomethine by a [4 + 2] cycloaddition reaction with the resulting aroylketenes. In the course of this reaction 6-aryl-3-cyanomethyl-3,4-

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dihydro-2H-1,3-oxazin-4-ones are obtained [6]. 2-(Cyanoimino)-1,3-dithiolane under analogous conditions reacts with its own C≡N bond giving the corresponding 4H-1,3-oxazin-4-ones [7].

The aim of the present work is the investigation of the interaction of 5-aryl-2,3-dihydrofuran-2,3-diones **1** with S-methyl-N-cyano-N'-phenylisothioureas **3** (R^2 = SMe, R^3 = NHPh), N-cyano[di(methylthio)]-imidocarbonate **4** $R^2 = R^3$ = SMe), N-cyano-N',N'-dimethylformamidine **5** (R^2 = H, R^3 = NMe_2), containing the N≡C–N=C fragment, and N,N-bis(β-cyanoethyl)cyanamide **6**, having nonequivalent C≡N bonds, and also modeling their reactions with aroylketenes using methods of quantum chemistry.

We established that as a result of briefly boiling equimolar amounts of compounds **1a,b** and **3** in toluene 6-aryl-2-[(methylthio)(phenylamino)methylene]amino-4H-1,3-oxazin-4-ones **7a,b** are formed. Melting points, yields, and data of elemental analysis of the compounds synthesized are given in Table 1, and spectral characteristics in Table 2.

The scheme of forming oxazines **7** includes thermal decarbonylation of furandiones **1** and a [4 + 2] cycloaddition reaction of aroylketenes **2** at the C≡N bond of compound **3**. Products of addition of aroylketenes at the C=N bond of isourea **3**, the substituted 3,4-dihydro-2H-1,3-oxazin-4-ones **8,** were not detected in the reaction mixture.

Boiling equimolar amounts of compounds **1** and **4** in toluene did not lead to the expected 6-aryl-2-[di(methylthio)methylen]amino-4H-1,3-oxazin-4-one **10** nor to the alternative 3,4-dihydro-2H-1,3-oxazin-4-one **11**. From the reaction mixture only dimers of aroylketenes **9**, identified by comparison with known samples [1], were isolated. The fact is that 2-(cyanoimino)-1,3-dithiolane, the electronic analog of compound **4**, interacts with furandione **1** under analogous conditions at the C≡N bond with the formation of [4 + 2] cycloadducts [7].

N-Cyanoamidine **5** reacts with ketenes **2**, generated by thermolysis of furandiones **1**, also at its C≡N bond. The structure of the reaction products, 6-aryl-2-dimethylaminomethyleneamino-4H-1,3-oxazin-4-ones **12a,b**, was established by X-ray structural analysis (XSA) [10]. As in the cases considered previously the formation of substituted 3,4-dihydro-2H-1,3-oxazin-4-ones **13** was not observed.

Aroylketenes **2**, generated by thermolysis of furandiones **1**, add exclusively at the N–C≡N bond of N,N-bis(β-cyanoethyl)cyanamide **6** with the formation of 6-aryl-2-[N,N-bis(β-cyanoethyl)amino]-4H-1,3-oxazin-4-ones **14a-d**. Other [4 + 2] cycloadducts (such as type **15**) were not detected in the reaction mixture.

TABLE 1. Physicochemical Properties of Compounds **7**, **12**, and **14**

Compound	Empirical formula	Found, % Calculated, % C	 H	 N	mp, °C	Yield, %
7a	$C_{18}H_{15}N_3O_2S$	64.0 64.1	4.3 4.5	12.4 12.5	190-191	68
7b	$C_{19}H_{17}N_3O_2S$	64.8 65.0	4.7 4.8	11.7 12.0	184-185	62
12a	$C_{13}H_{13}N_3O_2$	64.0 64.2	5.2 5.3	17.1 17.3	204-205	67
12b	$C_{14}H_{15}N_3O_2$	65.4 65.2	5.8 5.7	16.3 16.2	195-197	70
14a	$C_{16}H_{14}N_4O_2$	65.3 65.3	4.6 4.7	19.1 19.1	145-147	98
14b	$C_{17}H_{16}N_4O_2$	66.3 66.2	5.4 5.2	18.2 18.2	179-180	85
14c	$C_{17}H_{16}N_4O_3$	63.2 63.0	4.9 4.9	17.5 17.3	220-221	83
14d	$C_{16}H_{13}ClN_4O_2$*	58.4 58.5	4.2 4.0	17.2 17.1	195-196	80

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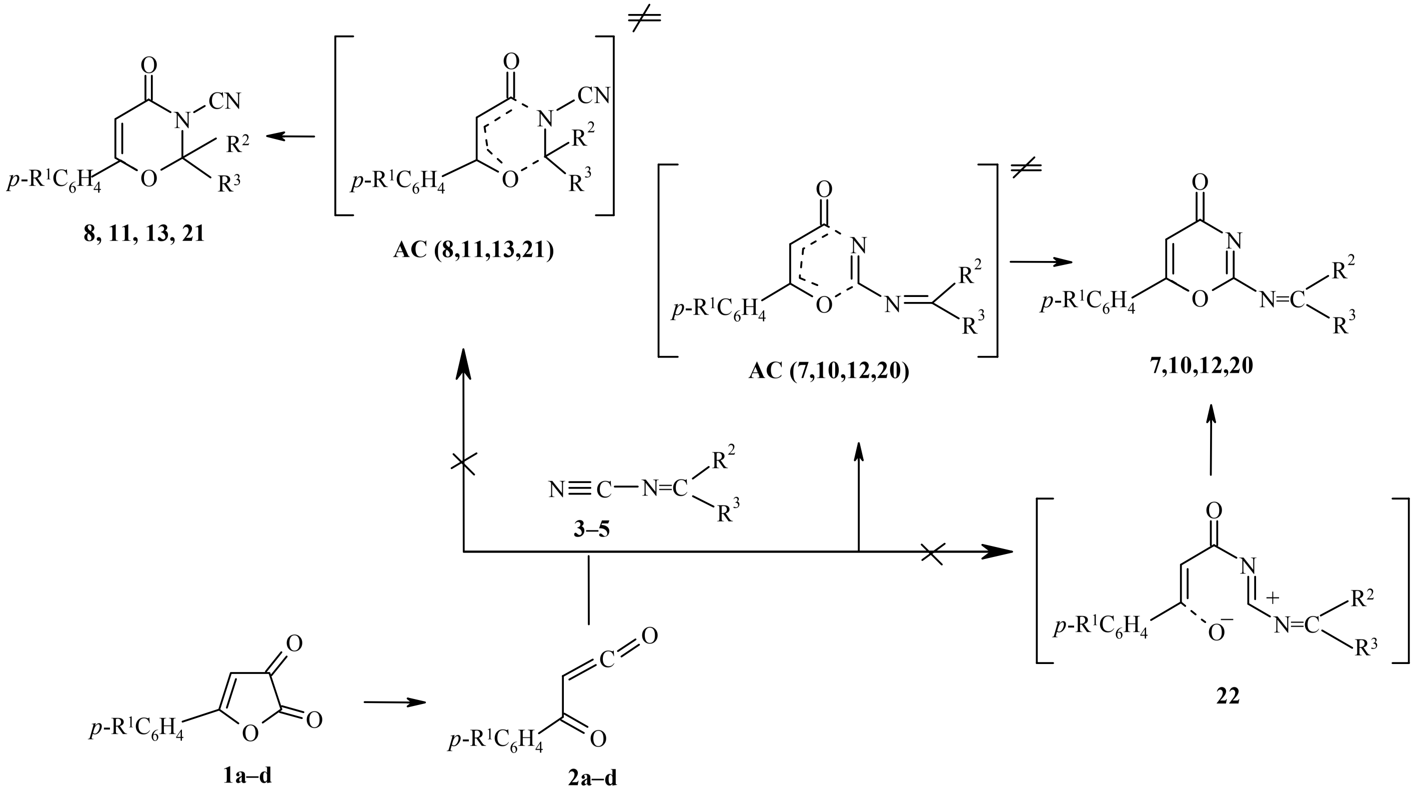
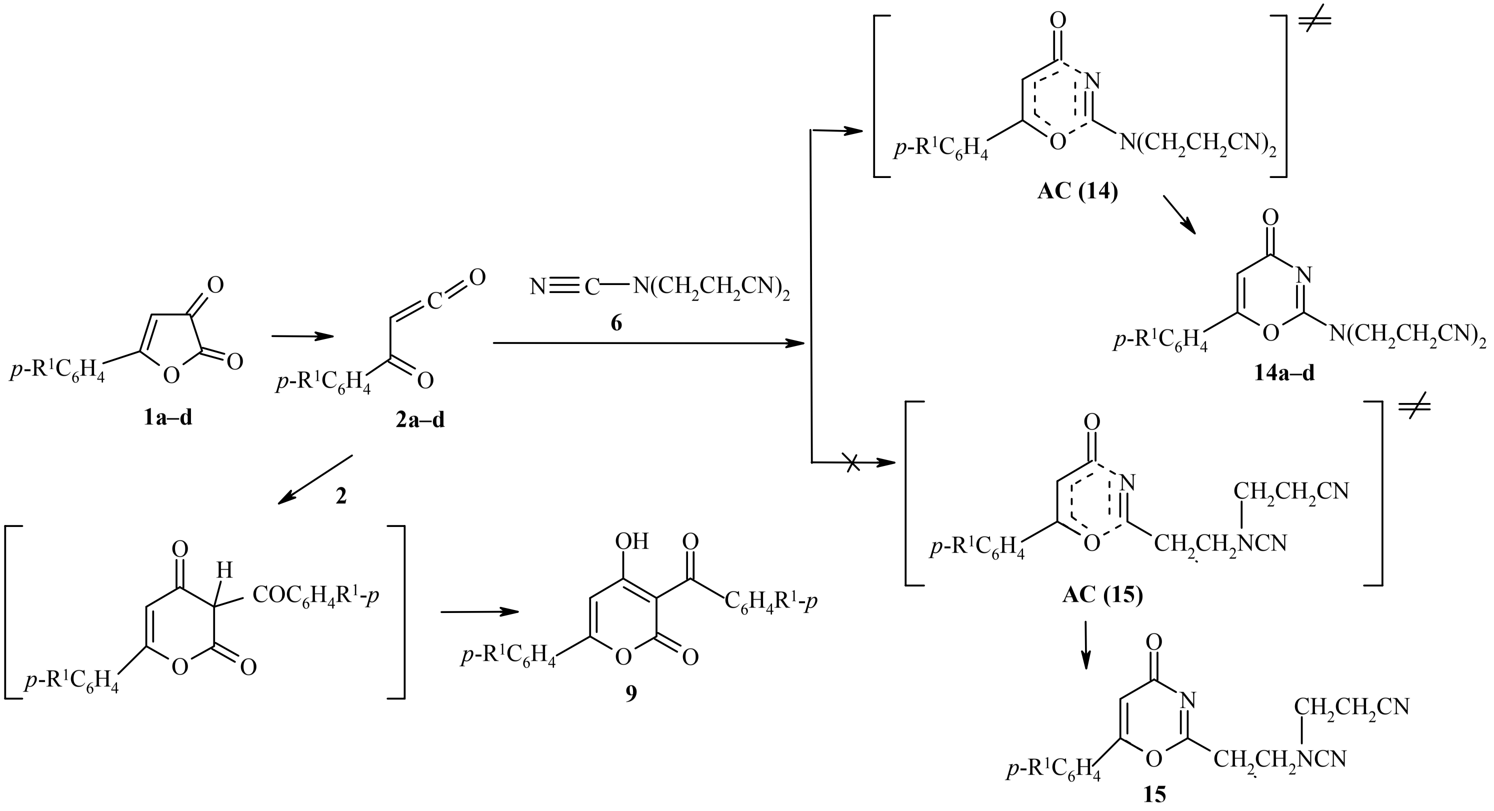
* Found, %: Cl 10.9; calculated, %: Cl 10.8.

Scheme 1



1, 7, 12 a $R^1 = H$, **b** $R^1 = Me$, **c** $R^1 = MeO$, **d** $R^1 = Cl$; **3** $R^2 = SMe$, $R^3 = NHPh$ **4** $R^2 = R^3 = SMe$; **5** $R^2 = H$, $R^3 = NMe_2$
AC is activated complex

Scheme 2



1, 14 a $R^1 = H$, **b** $R^1 = Me$, **c** $R^1 = MeO$, **d** $R^1 = Cl$; **3** $R^2 = SMe$, $R^3 = NHPh$; **4** $R^2 = R^3 = SMe$; **5** $R^2 = H$, $R^3 = NMe_2$

AC is activated complex

TABLE 2. Spectral Characteristics of Compounds **7**, **12**, and **14**

Compound	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm (*J*, Hz)
7a	1640, 1670, 3060	2.5 (1H, s, SCH_3); 6.4 (1H, s, CH=C); 7.0-7.9 (10H, m, $2C_6H_5$); 12.7 (1H, s, NH)
7b	1650, 1675, 3090	2.4 (1H, s, CH_3); 2.5 (1H, s, SCH_3); 6.4 (1H, s, CH=C); 7.0-7.8 (9H, m, C_6H_4, C_6H_5); 12.8 (1H, s, NH)
12a	1620-1660, 3060	3.06 (3H, s, CH_3); 3.20 (3H, s, CH_3); 6.5 (1H, s, CH=C); 7.35-7.95 (5H, m, C_6H_5); 8.68 (1H, s, N=CH)
12b	1610-1630, 1670, 3060	2.29 (3H, s, CH_3); 3.04 (3H, s, CH_3); 3.18 (3H, s, CH_3); 6.49 (1H, s, CH=C); 7.28 (2H, d, J_o = 8.3, H-3 arom.); 7.73 (2H, d, J_o = 8.3, H-2 arom.); 8.66 (1H, s, N=CH)
14a	1650-1670, 2280, 3090	2.9 (2H, t, J_{HH} = 6.8, CH_2); 3.8 (2H, t, J_{HH} = 6.8, CH_2); 6.55 (1H, s, CH=C); 7.4-7.8 (5H, m, C_6H_5)
14b	1655, 2275, 3080	2.3 (3H, s, CH_3); 2.9 (2H, t, J_{HH} = 6.8, CH_2); 3.8 (2H, t, J_{HH} = 6.8, CH_2); 6.45 (1H, s, CH=C); 7.25 (2H, d, J_o = 8.0, H-3 arom.); 7.70 (2H, d, J_o = 8.0, H-2 arom.)
14c	1630-1660, 2267, 3080	2.9 (2H, t, J_{HH} = 6.8, CH_2); 3.8 (2H, t, J_{HH} = 6.8, CH_2); 3.85 (3H, s, OCH_3); 6.4 (1H, s, CH=C); 7.25 (2H, d, J_o = 9.0, H-3 arom.); 7.60 (2H, d, J_o = 9.0, H-2 arom.)
14d	1655-1675, 2275, 3080	2.9 (2H, t, J_{HH} = 6.8, CH_2); 3.8 (2H, t, J_{HH} = 6.8, CH_2); 6.5 (1H, s, CH=C); 7.25 (2H, d, J_o = 9.0, H-3 arom.); 7.70 (2H, d, J_o = 9.0, H-2 arom.)

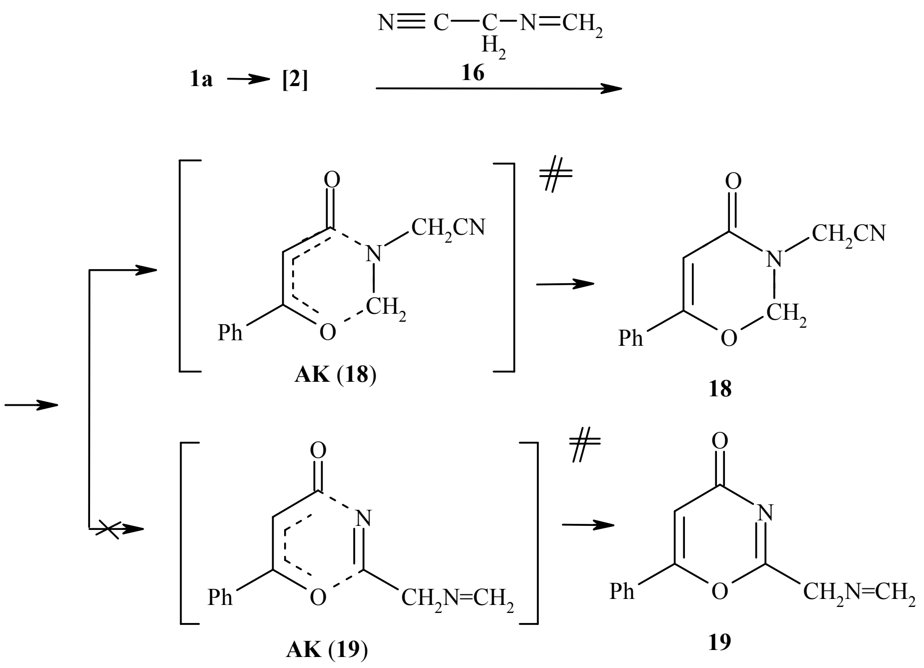
With the aim of explaining the results of this investigation and of data obtained previously [6, 7] we have carried out calculations of the electronic structure of the molecules of cyano compounds **3-6**, and also of the above-mentioned methylenaminoacetonitrile **16** and 2-(cyanoimino)-1,3-dithiolane **17** by the semiempirical SSP MO LCAO method using the MNDO-PM3 approach [11].

However the distribution of electron density in the molecules of the cyano compounds, as it turned out, did not permit an explanation of their behavior in reactions with ketenes **2**. Among the static reactivity indexes of cyano compounds **3-6**, **16**, **17** (total and π-electron charges on nitrogen atoms and the populations of its AO) it was not possible to find any index, analysis of which would permit arranging these cyano compounds in a series of increasing (or decreasing) activity in relation to aroylketenes.

According to the calculation, the negative charge on the carbon atom of the cyano group is greater than that on the nitrogen atom, which seems very unlikely in view of the electronegativity of these atoms. In cyano compounds **3-5** it turned out that the sp^2-hybridized nitrogen atom, according to the calculation, has more electron excess than the *sp*-hybridized, although the aroylketene molecule attacks just the latter. The sizes of the charges on atoms depends essentially on the approach used for the calculation. Thus the charges on the atoms of the N≡C–N fragment of the compound **5** molecule, according to semiempirical calculations, in the various approaches were: CNDO/2 [-0.212, +0.152, -0.199 arbitrary units (a. e.)], MNDO (-0.128, +0.002, -0.269 a. e.), AM1(-0.084, -0.068, -0.212 a. e.), MNDO-PM3 (-0.099, -0.107, -0.050 a. e.).

In the benzoylketene **2a** molecule the total/π-electron charges on atoms have the following values: $C_{(1)}=\underline{O}$ (-0.144/+0.303), $C_{(1)}$ (+0.417/+0.163), $C_{(2)}$ (-0.488/-0.382), $C_{(3)}$ (+0.426/+0.276). $C_{(3)}=\underline{O}$ (-0.364/-0.391). The total/π-electron bond orders are equal to: 2.119/0.592 [$C_{(1)}=O$], 1.591/0.764 [$C_{(1)}=C_{(2)}$], 0.987/0.317 [$C_{(2)}–C_{(3)}$], 1.835/0.864 [$C_{(3)}=O$]. (The calculated data published in [12] do not contain values for atomic charges and bond orders)

Since the static indexes of reactivity of the cyano compounds were unable to explain the observed results we localized the transition states of the [4 + 2] cycloaddition reactions of ketene **2a** with cyano compounds **3-6** and the energies of activation were assessed (E_a) as the difference of the enthalpies of formation of the activated complexes [ΔH_f(**AC**)] and the initital reactants benzoylketene **2a** and the cyano compound (CC) [ΔH_f(**2a**)] – [ΔH_f(CC)].



With the aim of clarifying the suitability of the MNDO-PM3 approach for solving this problem, we have localized the transition states of the model reactions of ketene **2a** with methyleneaminoacetonitrile **16** leading respectively to 3-cyanomethyl-6-phenyl-3,4-dihydro-2H-1,3-oxazin-4-one **18** and 2-methyleneaminomethyl-6-phenyl-4H-1,3-oxazin-4-one **19**.

The correctness of the localization of the transition states is confirmed by one negative value of the Hesse matrix. According to the calculation the activation barrier for the reaction forming oxazine **18** (56.0 kJ/mole) is less than for forming oxazine **19** (72.3 kJ/mol), which is not contrary to the experimental data [6]. The calculated energy of activation for the reaction forming cycloadduct **20** ($R^2 + R^3 = –SCH_2CH_2S–$) from ketene **2a** and cyano compound **17** (73.3 kJ/mol) proved to be not only lower than that of the alternative cycloadduct **21** ($R^2 + R^3 = –SCH_2CH_2S–$) (135.4 kJ/mol), but also lower than the energy of activation of the dimerization reaction of ketene **2a** (94.6 kJ/mol) [13], which explains the predominant formation of the cycloadduct and not the dimer.

The calculated energies of activation of the reactions investigated in the present study are given in Table 3.

As follows from the calculations, the values of E_a of all the reactions are less than the values of E_a for the dimerization reaction of ketene **2a**. This also indicates the preference to form cycloadducts **7**, **10**, **12**, and **14**. The reasons for the passive nature of cyano compound **4** in the reaction with compound **2a** prior to the end are not clear, since the interaction of compound **2a** and **17,** characterized by a higher calculated energy of activation, leads to the formation of a 1,3-oxazine.

The hypothesis was expressed previously that the interaction of aroylketenes with cyano compounds leading to substituted 4H-1,3-oxazin-4-ones is a coordinated [4π + 2π] cycloaddition reaction [6]. The putting into practice of such a mechanism requires the drawing together of the reactants in parallel planes [14] and the formation of new bonds through the π-electron systems of the diene (aroylketene) and the dienophile (cyano compound). However to localize the transition state in such an approach of reactants was unsuccessful. It turned out that the activated complexes corresponding to the transition state of the reaction of ketene **2a** with the enumerated cyano compounds have a completely different geometry. Their main geometric parameters (bond lengths and valence angles) are given in Table 4.

TABLE 3. Enthalpies of Formation (ΔH_f), Energies of Activation (E_a), Bond Lengths (l, Å), Valence Angles (ω, deg) in the Activated Complexes (**AC**) of the Reaction of Benzoylketene with Cyano Compounds **3-6**

Parameter	**AC (7)**	**AC (10)**	**AC (20)**	**AC (12)**	**AC (14)**
ΔH_f, kJ/mol	304.4	230.9	289.0	176.9	385.6
Ea, kJ/mol	21.3	65.2	73.3	42.9	61.1
O(1)···C(2)	2.046	2.087	2.084	2.068	2.111
C(2)–N(3)	1.209	1.195	1.192	1.201	1.191
N(3)···C(4)	1.488	1.520	1.527	1.502	1.535
C(4)–C(5)	1.422	1.406	1.403	1.413	1.402
C(5)–C(6)	1.371	1.411	1.415	1.405	1.415
C(6)–O(1)	1.280	1.265	1.262	1.268	1.262
C(4)=O	1.212	1.210	1.209	1.212	1.209
O(1)···C(2)–N(3)	100.9	98.4	98.3	100.0	98.6
C(2)–N(3)···C(4)	139.0	142.5	142.8	140.6	141.7
N(3)···C(4)–C(5)	115.0	112.9	112.3	114.0	113.3
C(4)–C(5)–C(6)	125.1	125.7	125.9	125.2	126.3
C(5)–C(6)–O(1)	123.4	123.8	123.8	123.7	123.4
C(6)–O(1)···C(2)	117.1	116.7	116.7	116.5	116.8
N(3)···C(4)=O	113.2	112.4	112.4	112.8	111.3
C(5)–C(4)=O	131.9	134.8	134.4	133.3	135.4
ΔlO(1)–C(2)	0.67	0.66	0.66	0.66	0.64
ΔlC(2)=N(3)	1.09	1.09	1.10	1.09	1.10
ΔlN(3)–C(4)	0.97	0.95	0.94	0.96	0.94
ΔlC(4)–C(5)	1.03	1.05	1.05	1.04	1.05
ΔlC(5)=C(6)	0.99	0.96	0.96	0.96	0.96
ΔlC(6)–O(1)	1.08	1.09	1.10	1.10	1.10
ΔlC(4)=O	1.00	1.00	1.00	1.00	1.00

As follows from the calculations, the activated complexes of the reactions of benzoylketene **2a** with cyano compounds **3-6** are practically planar. The dihedral angles have the following values.

$$\theta\ O_{(1)}–C_{(2)}–N_{(3)}–C_{(4)} = 1.5\pm1.1°,\ \theta\ C_{(2)}–N_{(3)}–C_{(4)}–C_{(5)} = 2.5\pm2.0°,$$
$$\theta\ N_{(3)}–C_{(4)}–N_{(5)}–C_{(6)} = 1.2\pm1.2°,\ \theta\ C_{(4)}–C_{(5)}–C_{(6)}–O_{(1)} = 0.6\pm0.1°,$$
$$\theta\ C_{(5)}–C_{(6)}–O_{(1)}–C_{(2)} = 1.4\pm1.0°,\ \theta\ C_{(6)}–O_{(1)}–C_{(2)}–N_{(3)} = 0.6\pm0.5°.$$

The interatomic distances $O_{(1)}\cdots C_{(2)}$ and $N_{(3)}\cdots C_{(4)}$ in the activated complexes were equal to 2.079±0.032 and 1.512±0.024 Å respectively, indicating the asynchronicity of forming the corresponding bonds, but within the limits for a coordinated process. Attempts to find a zwitter ion intermediate of type **22** on the potential energy surface of the reaction of ketene **2a** with cyano compounds **3-6** proved to be in vain.

Probably at the stage of forming activated complexes the $N_{(3)}–C_{(4)}$ bond is formed at an advanced time while at the stage of converting them into reaction products the $O_{(1)}–C_{(2)}$ bond is formed at an even higher rate. The $2p_y$ orbital of the $C_{(1)}$ atom of the benzoylketene **2a** molecule and the $2s$ orbital of the nitrogen atom of the cyano compound molecule participate in the formation of the $N_{(3)}–C_{(4)}$ bond. This is confirmed by the insignificant change in the C≡N bond length in the activated complexes compared with the isolated molecule of compounds **3-6** (the increase is no more than 4%). The total order of the $C_{(2)}=N_{(3)}$ bond in the activated complexes is on average 86% of the total C≡N bond order in the cyano compound molecules. Participation in the formation of the $N_{(3)}–C_{(4)}$ bond by $2p_z$ or $2p_y$ orbitals of the nitrogen atom would lead to a large increase in length and a reduction of the order of the C=N bond in the cyano fragment of the activated complexes. The $O_{(1)}–C_{(2)}$ bond is formed by overlap of orbitals of one of the lone electron pairs of the oxygen atom and the

TABLE 4. Total/π-Electron Charges of Atoms, Total/π-Electron Charges of Bonds Δ*p* in the Activated Complexes (**AC**) in the Reaction of Benzoylketene **2a** with Cyano Compounds **3-6**, **16**

Parameter*	AC (**7**)	AC (**10**)	AC (**20**)	AC (**12**)	AC (**14**)
$qO_{(1)}$	-0.565 -0.672	-0.517 -0.609	-0.497 -0.595	-0.541 -0.632	-0.531 -0.601
$qC_{(2)}$	+0.217 +0.134	+0.149 +0.101	+0.138 +0.106	+0.196 +0.123	+0.071 +0.064
$qN_{(3)}$	-0.020 +0.226	+0.037 -0.185	+0.057 -0.173	+0.009 -0.199	+0.074 -0.085
$qC_{(4)}$	+0.444 +0.239	+0.448 +0.226	+0.448 +0.223	+0.447 +0.231	+0.440 +0.212
$qC_{(5)}$	-0.558 -0.403	-0.586 -0.433	-0.587 -0.436	-0.582 -0.427	-0.589 -0.432
$qC_{(6)}$	+0.401 +0.267	+0.414 +0.287	+0.420 +0.291	+0.412 +0.280	+0.429 +0.297
$qC_{(4)}{=}\underline{O}$	-0.346 -0.455	-0.346 -0.509	-0.350 -0.509	-0.355 -0.483	-0.342 -0.506
$pO_{(1)}\cdots C_{(2)}$	0.154 0.092	0.136 0.092	0.140 0.094	0.145 0.096	0.118 0.092
$pC_{(2)}–N_{(3)}$	2.293 0.894	2.424 0.918	2.456 0.925	2.369 0.909	2.469 0.963
$pN_{(3)}\cdots C_{(4)}$	0.774 0.206	0.701 0.183	0.687 0.178	0.741 0.196	0.676 0.169
$pC_{(4)}–C_{(5)}$	1.140 0.451	1.214 0.522	1.233 0.537	1.186 0.496	1.239 0.542
$pC_{(5)}–C_{(6)}$	1.389 0.661	1.278 0.580	1.255 0.560	1.315 0.608	1.254 0.560
$pC_{(6)}–O_{(1)}$	1.399 0.615	1.514 0.692	1.538 0.706	1.481 0.671	1.529 0.703
$pC_{(4)}{=}O$	1.827 0.807	1.820 0.775	1.815 0.762	1.813 0.789	1.821 0.767
$\Delta pO_{(1)}–C_{(2)}$	0.15	0.13	0.14	0.14	0.12
$\Delta pC_{(2)}–N_{(2)}$	1.46	1.40	1.41	1.41	1.58
$\Delta pN_{(3)}–C_{(4)}$	0.75	0.73	0.72	0.76	0.70
$\Delta pC_{(4)}–C_{(5)}$	1.17	1.25	1.27	1.22	1.27
$\Delta pC_{(5)}–C_{(6)}$	0.79	0.73	0.71	0.75	0.71
$\Delta pC_{(6)}–O_{(1)}$	1.34	1.46	1.48	1.46	1.47
$\Delta pC_{(4)}{=}O$	0.99	0.97	0.97	0.98	0.99

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* π-Electron charges on oxygen atoms were determined as the difference between the calculated population of its $2p_z$-AO and 1.

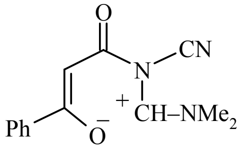
$2p_y$-orbitals of the carbon atom, which is indicated by the value of the $C_{(6)}–O_{(1)}\cdots C_{(2)}$ valence angle in the activated complexes being equal to 116.8±0.3°. The change in the geometry of the dienophile fragment compared with the isolated molecule is insignificant. Thus the $C_{(1)}–C_{(2)}$ bond length in the **2a** molecule [bond $C_{(4)}–C_{(5)}$ in the activated complex] is increased by 6.5±0.5%, the $C_{(2)}–C_{(3)}$ bond becomes shorter by 4.5±1.5%, and the C=O bond length is increased by 3 to 5%. The $C_{(2)}{=}C_{(1)}{=}O$ valence angle undergoes the greatest change. It is reduced from 179.1 to 133.7±1.8°. The valence angles $C_{(1)}{=}C_{(2)}–C_{(3)}$ and $C_{(2)}–C_{(3)}{=}O$ are increased insignificantly, by no more than 2.6°. The extent of bond formation in the activated complexes may be judged by the value of Δ*l*, the ratio of bond length in the cycloadduct to the analogous bond length (interatomic distance) in the activated complex (Table 3). As shown by the calculations, the $O_{(1)}\cdots C_{(2)}$ interatomic distance in the activated complexes is 64-67% of the lengths of the analogous bonds in the cycloadduct, but for $N_{(3)}\cdots C_{(4)}$ it is 94-97%. The lengths of the remaining bonds also did not undergo significant changes, as follows from comparison of the values of Δl. In parallel with Δl we calculated Δp as the ratio of bond order in the activated complex to the order of the analogous bond in the cycloadduct (Table 4). Analysis of these values, and also the values of the atomic charges, shows that the distribution of electron density in the activated complexes differs substantially from that in the cycloadducts. For example, Δp for the $O_{(1)}–C_{(2)}$ bond is on average14%, and Δp for the $N_{(3)}–C_{(4)}$ bond is 73%.

At the stage of forming the activated complexes a transfer occurs of from 0.450 elementary charge from the molecule of cyano compound to the ketene molecule **2a** in activated complex **AC** (**14**) to 0.503 elementary charge in activated complex **AC** (**7**). As calculations showed, a large portion of the charge (-0.203 a. u.) is taken by the ketenic oxygen atom and a lesser by the ketonic atom (-0.174 a. u.). The charge on the $C_{(2)}$ atom is increased insignificantly (-0.092 a. u.), and the *sp*-hybridized nitrogen atom in all the activated complexes, with the exception of **AC** (**6**), becomes electron-deficient.

According to the data of the calculations the energy of activation of the reaction forming oxazine **7** proved to be 63.1 kJ/mol less than for the hypothetical oxazine **8**.

According to the calculation, the formation of oxazines **8** and **11** when carrying out the corresponding processes may also occur in a coordinated manner. However the energy of activation of the reaction **2a** + **3** → **7** is 63.1 kJ/mole less than the reaction **2a** + **3** → **8a**, and oxazine **8a** is not formed. The difference in the energies of activation of the reactions forming oxazines **14a** and **15a** is 15.8 kJ/mol.

According to the calculations, the formation of oxazine **13a** from ketene **2a** and cyanoamidine **5** must proceed stepwise through zwitter ion **23**.



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But the energy profile of this reaction lies higher in the ΔH_f scale than the profile of the coordinated process of forming oxazine **12**, and oxazine **13** is not formed. Quantum chemical modeling of the reaction of benzoylketene **2a** with cyano compounds **3, 5, 6,** and **16** gives a qualitative agreement with experiment, but the reaction of furandiones **1** with cyano compounds **4** and **17** deserves a deeper study.

EXPERIMENTAL

The IR spectra of the synthesized compounds were recorded on a UR 20 spectrometer in nujol. The ^1H NMR spectra were obtained on a Tesla BS 487 (80 Hz) instrument in $CDCl_3$, internal standard was HMDS (δ 0.05 ppm). The progress of reactions and the purity of the compounds obtained were checked by TLC on Silufol plates in the system benzene–ether, 3:2, visualization was with iodine vapor.

The quantum chemical calculations were carried out with the aid of the MOPAC 7.0 [15] set of programs on a Pentium 200-MMX computer. Transition states were localized with the aid of the TS procedure and were refined with the aid of the NLLSQ procedure.

6-Aryl-2-[(methylthio)(phenylamino)methylene]amino-4H-1,3-oxazin-4-ones 7a,b. A mixture of furandione **1** (0.01 mol) and S-methyl-N-cyano-N'-phenylisothiourea **3** (0.01 mol) in anhydrous toluene (15-20 ml) was boiled for 30 min. The reaction mixture was cooled to room temperature, the precipitated solid filtered off, washed with ether, and recrystallized from toluene.

Interaction of 5-Aryl-2,3-dihydro-2,3-furandiones with N-Cyano[di(methylthio)]imidocarbonate. A mixture of furandione **1** (0.01 mol) and cyano compound **4** (0.01 mol) in toluene (20-25 ml) was boiled for 30 min. After cooling the reaction mixture to room temperature pyranone **9** was filtered off. The filtrate was evaporated, the residue was recrystallized from hexane, and the initial cyano compound **4** was isolated.

6-Aryl-2-dimethylaminomethylenamino-4H-1,3-oxazin-4-ones 12a,b were obtained analogously to compounds **7a,b** from furandiones **1** and N-cyano-N',N'-dimethylformamidine (**5**).

6-Aryl-2-[N,N-bis(β-cyanoethyl)amino]-4H-1,3-oxazin-4-ones 14a-d. N,N-Bis(β-cyanoethyl)-cyanamide **6** (0.01 mol) was added to a solution of furandione **1** (0.01 mole) in anhydrous dioxan (20-25 ml), and the mixture boiled for 1 h. The solid, precipitated on cooling the mixture to room temperature, was filtered off, and recrystallized from ethanol.

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