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STUDY OF REACTION OF 5-ARYL-2,3-DIHYDRO-2,3-FURANDIONES WITH N-CYANOTRIPHENYLPHOSPHINIMINE. MOLECULAR AND CRYSTAL STRUCTURE OF THE SOLVATE OF 6-*p*-TOLYL-2-TRIPHENYLPHOSPHINIMINO-4H-1,3-OXAZIN-4-ONE WITH ACETONITRILE

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We have used X-ray diffraction to establish the structure of 6-p-tolyl-2-triphenylphosphinimino-4H-1,3-oxazin-4-one. We have modeled its formation from 5-p-toluoylketene and N-cyanotriphenylphosphinimine using the semiempirical SCF MO LCAO method in the MNDO-PM3 approximation. We show that the reaction occurs according to a concerted mechanism.

Keywords: 5-aryl-2,3-dihydro-2,3-furandiones, 6-aryl-2-triphenylphosphinimino-4H-1,3-oxazin-4-ones, aroylketenes, N-cyanotriphenylphosphinimine, transition state, semiempirical SCF MO LCAO method, X-ray diffraction.

In a preliminary report [1], we hypothesized that the products of reaction between 5-aryl-2,3-dihydro-2,3-furandiones **1a,b** and N-cyanotriphenylphosphinimine (**3**) are 6-aryl-2-triphenylphosphinimino-4H-1,3-oxazin-4-ones **5a,b**.

In order to more reliably establish the structure of the products of this reaction, we carried out an X-ray diffraction study of a single crystal of 6-*p*-tolyl-2-triphenylphosphinimino-4H-1,3-oxazin-4-one (**5b**), which we found forms a solvate (1:1) with acetonitrile, the solvent used for recrystallization. The general form of the molecule is shown in Fig. 1; the bond lengths and bond angles are given in Tables 1 and 2, and the coordinates of the non-hydrogen atoms are given in Table 3.

The phosphorus atom has the usual distorted tetrahedral bond configuration. The P–$C_{(Ph)}$ distances 1.798(2)-1.816(2) Å (average 1.807(2) Å) are typical for four-coordinate phosphorus compounds [2]. The bond angles at the phosphorus atom are within the range 103.7(1)-117.3(1)°, and the average value of the C–$P_{(9)}$–$N_{(8)}$ angle (111.4(1)°) is somewhat greater than the C–$P_{(9)}$–C angle (107.3(3)°).

The $P_{(9)}$=$N_{(8)}$ bond length, equal to 1.619(1) Å, corresponds to a double bond. The bond angle $C_{(2)}$–$N_{(8)}$–$P_{(9)}$ is 118.9° and close to the standard value of 120° for an sp^2-hybridized atom. According to the known relationship between the bond angle at the nitrogen atom and the P=N bond length in phosphinimines [3], the value found for the angle at the $N_{(8)}$ atom should correspond to a P=N bond length of ~1.62 Å, which is also observed experimentally.

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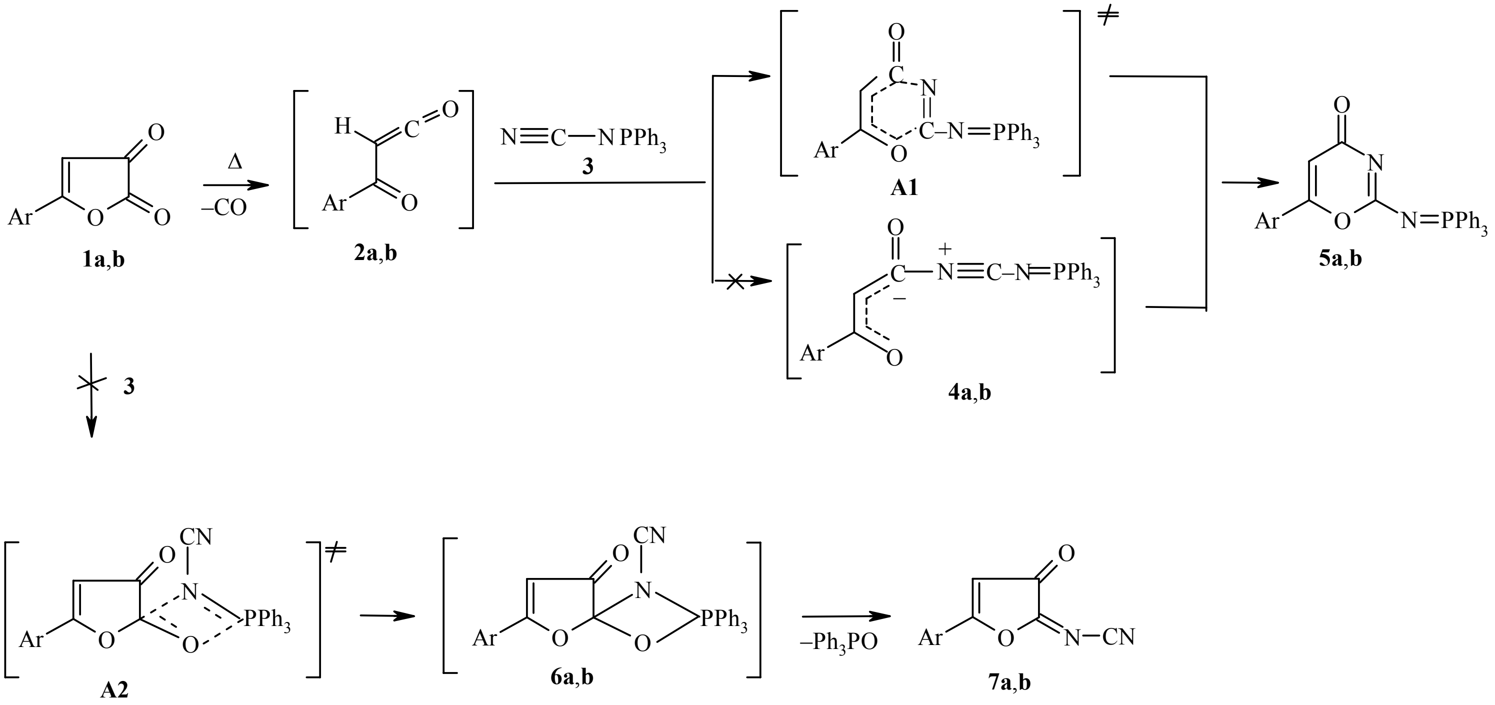
Scheme 1



1, **2**, **4**–**7** Ar = Ph, *p*-MeC_6P_4

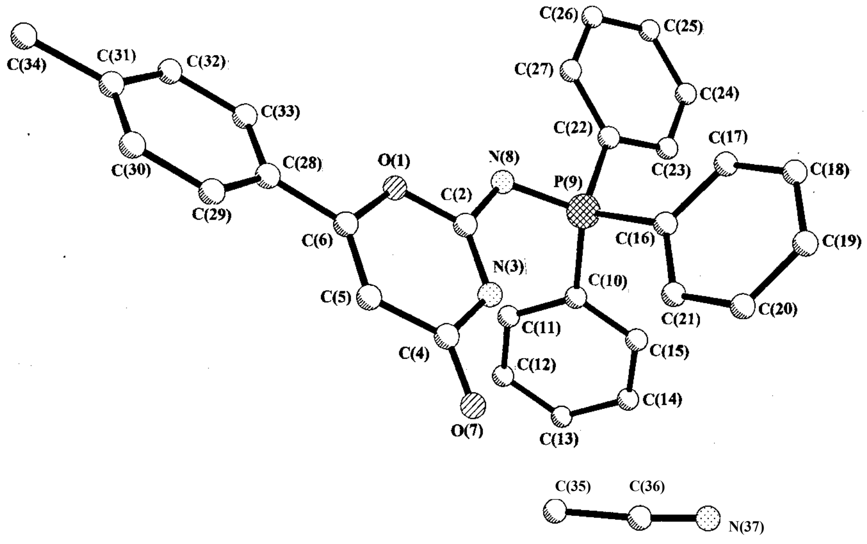


Fig. 1. Molecular structure of compound **5b**.

All the atoms forming the heterocycle are located in the same plane (within ~0.002 Å). The bond lengths in the heterocyclic moiety have intermediate values between single bond and double bond lengths, probably due to conjugation. The $C_{(2)}-N_{(8)}$ bond length (1.326(2) Å) is shorter than the length of the formally single bond $N(sp^2)-C(sp^2)$ (1.43 Å) [4], and has a partially double bond character (its π-bond order, estimated from the bond length *vs*. bond order graph in [5], is ~0.54). The intracyclic angle $O_{(1)}-C_{(2)}-N_{(3)}$ is increased up to 123.6(2)°, but the planarity of the bonds formed by the $C_{(2)}$ is retained.

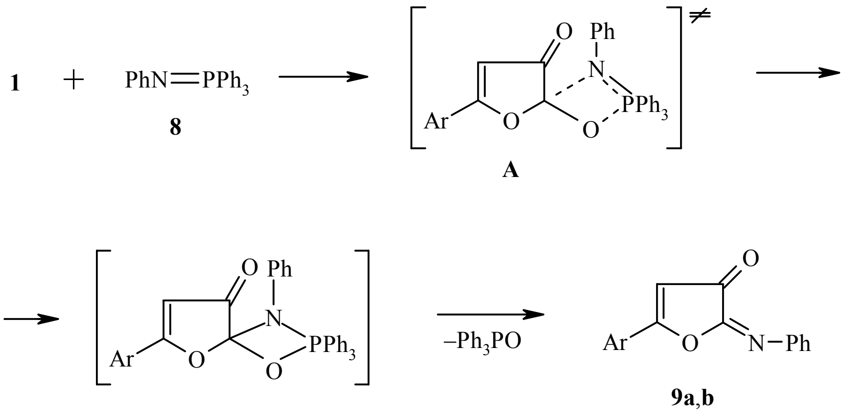
The torsional angles $P_{(9)}=N_{(8)}-C_{(2)}=N_{(3)}$ and $P_{(9)}=N_{(8)}-C_{(2)}-O_{(1)}$ are equal respectively to -2.6(3) and 177.2(1)°, i.e., the $P_{(9)}=N_{(8)}$ bond is slightly turned away from the plane of the heterocycle and has a *trans* orientation relative to the $O_{(1)}-C_{(2)}$ bond. The deviation of the $N_{(8)}$ and $P_{(9)}$ atoms from the plane of the heterocycle is 0.087 Å and 0.192 Å, which allows for the possibility of conjugation between the heterocycle and the $N_{(8)}=P_{(9)}$ bond.

The bond lengths and bond angles in the phenyl substituents have the typical values and do not require any commentary. The orientation of the phenyl substituents at the phosphorus is propeller-like, and the dihedral angles between the planes of the phenyl rings are: $C_{(10)}\cdots C_{(15)}/C_{(16)}\cdots C_{(21)}$ 65.1°, $C_{(10)}\cdots C_{(15)}/C_{(22)}\cdots C_{(27)}$ 72°, $C_{(16)}\cdots C_{(21)}/C_{(22)}\cdots C_{(27)}$ 70.6°.

The scheme for formation of 1,3-oxazines **5a,b** includes thermal decarbonylation of furandiones **1a,b** [6], leading to generation of aroylketenes **2a,b** [7] which then react with cyanoimine **3**. The reaction of compounds **2** and **3** may occur in a concerted manner (with participation of the activated complex **A1a,b**) or stepwise through the nitrilium form **4a,b**. We should note that obtaining substituted 1,3-oxazines **5a,b** in the reaction of furandiones **1** with N-cyanoimine **3** is rather unexpected. In fact, furandiones **1** react with compounds containing the P=N bond, for example N-phenyltriphenylphosphinimine (**8**) (Scheme 2), at temperatures lower than needed for thermal decarbonylation, and yield 5-aryl-2-(N-phenylimino)-2,3-dihydro-3-furanones (**9**) [8]. For this reason, formation of 5-aryl-2-(N-cyanoimino)-2,3-dihydro-3-furanones (**7a,b**) was more justifiable in the reaction under discussion, but they were not observed among the reaction products.

With the aim of determining the mechanism of the reaction of compounds **1** and **3**, we used the semiempirical SCF MO LCAO method to perform calculations for the molecules and also possible intermediates and activated complexes participating in this conversion. We first calculated the geometry of the 1,3-oxazine molecule **5b** in the MNDO [9], AM1 [10], and MNDO-PM3 [11] approximations (Table 4).

Scheme 2



9 Ar = Ph, p-MeC_6H_4

According to the data obtained, all the approximations used satisfactorily describe the geometry of the heterocyclic moiety of the molecule, but the AM1 approximation significantly overestimates the size of the bond angle $C_{(2)}$–$N_{(8)}$=$P_{(9)}$ (162.6°) and predicts values for the $N_{(8)}$=$P_{(9)}$ bond length (1.477 Å) and the $P_{(9)}$–C bond length (from 1.622 Å to 1.627 Å) that are too low. This approximation probably should not be used in calculations for molecules containing the indicated bonds.

The overestimation of the repulsion between nonvalence bonded atoms that is typical for the MNDO approximation is expressed in the substantial rotation of the *p*-tolyl moiety relative to the heterocyclic moiety. For this reason, in the following we used the MNDO-PM3 approximation. Since we could not find data on the electronic structure of compound **3** in the literature, we also performed the calculation for this molecule. We also performed the calculation in parallel for the N-phenyltriphenylphosphinimine **8** molecule which, as was shown earlier, reacts with 5-aryl-2,3-dihydro-2,3-furandiones as a nucleophile according to the Staudinger reaction scheme [8].

TABLE 1. Basic Bond Lengths (d) in the **5b** Molecule According to X-ray Diffraction Data

Bond	d, Å	Bond	d, Å	Bond	d, Å
$O_{(1)}$–$C_{(2)}$	1.384(2)	$C_{(10)}$–$C_{(15)}$	1.391(2)	$C_{(23)}$–$C_{(24)}$	1.386(3)
$O_{(1)}$–$C_{(6)}$	1.377(2)	$C_{(11)}$–$C_{(12)}$	1.385(3)	$C_{(24)}$–$C_{(25)}$	1.379(3)
$C_{(2)}$–$N_{(3)}$	1.305(2)	$C_{(12)}$–$C_{(13)}$	1.383(3)	$C_{(25)}$–$C_{(26)}$	1.388(3)
$C_{(2)}$–$N_{(8)}$	1.362(2)	$C_{(13)}$–$C_{(14)}$	1.388(4)	$C_{(26)}$–$C_{(27)}$	1.391(3)
$N_{(3)}$–$C_{(4)}$	1.376(2)	$C_{(14)}$–$C_{(15)}$	1.389(3)	$C_{(28)}$–$C_{(29)}$	1.387(3)
$C_{(4)}$–$C_{(5)}$	1.457(2)	$C_{(16)}$–$C_{(17)}$	1.408(3)	$C_{(28)}$–$C_{(33)}$	1.379(3)
$C_{(4)}$–$O_{(7)}$	1.232(3)	$C_{(16)}$–$C_{(21)}$	1.389(3)	$C_{(29)}$–$C_{(30)}$	1.392(3)
$C_{(5)}$–$C_{(6)}$	1.331(3)	$C_{(17)}$–$C_{(18)}$	1.386(3)	$C_{(30)}$–$C_{(31)}$	1.372(4)
$C_{(6)}$–$C_{(28)}$	1.477(2)	$C_{(18)}$–$C_{(19)}$	1.383(3)	$C_{(31)}$–$C_{(32)}$	1.378(4)
$N_{(8)}$–$P_{(9)}$	1.619(1)	$C_{(19)}$–$C_{(20)}$	1.388(3)	$C_{(31)}$–$C_{(34)}$	1.514(3)
$P_{(9)}$–$C_{(10)}$	1.807(2)	$C_{(20)}$–$C_{(21)}$	1.386(4)	$C_{(32)}$–$C_{(33)}$	1.395(3)
$P_{(9)}$–$C_{(16)}$	1.816(2)	$C_{(22)}$–$C_{(23)}$	1.401(2)	$C_{(35)}$–$C_{(36)}$	1.458(6)
$P_{(9)}$–$C_{(22)}$	1.798(2)	$C_{(22)}$–$C_{(27)}$	1.390(3)	$C_{(36)}$–$C_{(37)}$	1.110(4)
$C_{(10)}$–$C_{(11)}$	1.392(3)				

TABLE 2. Basic Bond Angles (ω) in the **5b** Molecule According to X-ray Diffraction Data

Angle	ω, deg	Angle	ω, deg.	Angle	ω, deg.
$O_{(1)}-C_{(2)}-N_{(3)}$	123.6(2)	$P_{(9)}-C_{(10)}-C_{(11)}$	118.8(1)	$C_{(17)}-C_{(18)}-C_{(19)}$	121.0(2)
$O_{(1)}-C_{(2)}-C_{(8)}$	110.6(1)	$P_{(9)}-C_{(10)}-C_{(15)}$	121.8(2)	$C_{(18)}-C_{(19)}-C_{(20)}$	119.7(2)
$O_{(1)}-C_{(6)}-C_{(5)}$	120.4(1)	$P_{(9)}-C_{(16)}-C_{(17)}$	120.0(2)	$C_{(19)}-C_{(20)}-C_{(21)}$	120.0(2)
$O_{(1)}-C_{(6)}-C_{(28)}$	112.3(2)	$P_{(9)}-C_{(16)}-C_{(21)}$	120.9(2)	$C_{(22)}-C_{(23)}-C_{(24)}$	119.6(2)
$C_{(2)}-O_{(1)}-C_{(5)}$	118.1(1)	$P_{(9)}-C_{(22)}-C_{(23)}$	120.0(1)	$C_{(22)}-C_{(27)}-C_{(26)}$	119.8(2)
$C_{(2)}-N_{(3)}-C_{(4)}$	120.3(1)	$P_{(9)}-C_{(22)}-C_{(27)}$	120.1(1)	$C_{(23)}-C_{(22)}-C_{(27)}$	119.8(2)
$C_{(2)}-N_{(8)}-P_{(9)}$	118.9(1)	$C_{(10)}-P_{(9)}-C_{(16)}$	106.8(1)	$C_{(23)}-C_{(24)}-C_{(25)}$	120.5(2)
$N_{(3)}-C_{(2)}-N_{(8)}$	125.1(1)	$C_{(10)}-P_{(9)}-C_{(22)}$	108.3(1)	$C_{(24)}-C_{(25)}-C_{(26)}$	120.1(2)
$N_{(3)}-C_{(4)}-C_{(5)}$	117.0(2)	$C_{(10)}-C_{(11)}-C_{(12)}$	120.3(2)	$C_{(25)}-C_{(26)}-C_{(27)}$	120.1(2)
$N_{(3)}-C_{(4)}-O_{(7)}$	120.3(1)	$C_{(10}-C_{(15)}-C_{(14)}$	120.2(2)	$C_{(28)}-C_{(29)}-C_{(30)}$	120.0(2)
$C_{(4)}-C_{(5)}-C_{(6)}$	120.5(2)	$C_{(11)}-C_{(10)}-C_{(15)}$	119.3(2)	$C_{(28)}-C_{(33)}-C_{(32)}$	120.5(2)
$C_{(5)}-C_{(4)}-O_{(7)}$	122.7(2)	$C_{(11)}-C_{(12)}-C_{(13)}$	120.3(2)	$C_{(29)}-C_{(28)}-C_{(33)}$	118.6(2)
$C_{(5)}-C_{(6)}-C_{(28)}$	127.3(2)	$C_{(12)}-C_{(13)}-C_{(14)}$	119.8(2)	$C_{(29)}-C_{(30)}-C_{(31)}$	121.8(2)
$C_{(6)}-C_{(28)}-C_{(29)}$	120.0(2)	$C_{(13)}-C_{(14)}-C_{(15)}$	120.0(2)	$C_{(30)}-C_{(31)}-C_{(32)}$	117.9(2)
$C_{(6)}-C_{(28)}-C_{(33)}$	121.4(2)	$C_{(16)}-P_{(9)}-C_{(22)}$	106.9(1)	$C_{(30)}-C_{(31)}-C_{(34)}$	120.6(2)
$N_{(8)}-P_{(9)}-C_{(10)}$	113.3(1)	$C_{(16)}-C_{(17)}-C_{(18)}$	119.5(2)	$C_{(31)}-C_{(32)}-C_{(33)}$	121.2(2)
$N_{(8)}-P_{(9)}-C_{(16)}$	117.3(1)	$C_{(16)}-C_{(21)}-C_{(20)}$	120.7(2)	$C_{(32)}-C_{(31)}-C_{(34)}$	121.5(2)
$N_{(8)}-P_{(9)}-C_{(22)}$	103.7(1)	$C_{(17)}-C_{(16)}-C_{(21)}$	119.1(2)	$C_{(35)}-C_{(36)}-C_{(37)}$	175.2(5)

According to the calculations, in the molecule of compound **3** the nitrogen atoms are characterized by the following values of the charges: -0.241 (N-nitrile) and -0.621 (N-imine). For comparison, the nitrogen atom in imine **8** has a large partial negative charge (-0.718). The highest occupied molecular orbital (HOMO) of the cyanoimine molecule **3** lies lower on the energy scale than the HOMO of imine **8** (the corresponding values are equal to -8.69 and -7.47 eV). These indices characterize N-cyanotriphenylphosphinimine (**3**) as a less effective nucleophile compared with compound **8**, and the passivity of the former in a Staudinger type reaction with 5-aryl-2,3-dihydro-2,3-furandiones becomes understandable to some extent.

As noted above, the absolute value of the negative charge on the nitrile nitrogen atom of the cyanoimine molecule **3** is less than the charge on the imine atom. However, the occupancy of the 2*s*-AO of the nitrile nitrogen atom, on which the unshared electron pair is located (1.771), is higher than for the imine nitrogen atom (1.702). This is important to bear in mind, assuming that their unshared electron pairs participate in formation of new bonds by these atoms.

Since the static electronic indices of the nitrogen atoms of the cyanoimine molecule **3** do not allow us to confidently predict the chemical behavior of this molecule, we modeled the reaction of aroylketenes **2a,b** with imine **3**. According to current opinion, the reaction of aroylketenes with compounds containing a C≡N bond is a concerted $[\pi^4 s + \pi^2 s]$ cycloaddition reaction [12]. This mechanism assumes that the reagents approach each other in parallel planes.

However, we could not localize the transition state for this type of approach of the reagents. We found that the activated complex corresponding to the transition state for the reaction (the correct localization of which is supported by the one negative value of the Hesse matrix) has a quite different geometry (the basic bond lengths, bond angles, and dihedral angles are given in Table 5). As follows from the calculations, the $O_{(1)}$, $C_{(2)}$, $C_{(4)}$, $C_{(5)}$, and $C_{(6)}$ atoms lie practically in one plane, while the $N_{(3)}$ atom deviates from that plane by 0.1 Å. The interatomic distances $O_{(1)}\cdots C_{(2)}$ and $N_{(3)}\cdots C_{(4)}$ in the activated complexes suggest that formation of the indicated bonds is an asynchronous but concerted process.

Attempts to look for a zwitterionic intermediate of the nitrilium cation type **4** proved to be unsuccessful. Probably in the step of formation of the activated complex, the $N_{(3)}\cdots C_{(4)}$ bond is formed at a faster pace, while in the step of its conversion to the reaction product the $O_{(1)}\cdots C_{(2)}$ bond is formed faster.

TABLE 3. Coordinates of Non-hydrogen Atoms (×10) of the **5b** Molecule and Their Equivalent Isotropic Temperature Factors (×10^3)

Atom	x	y	z	U, Å^2
$\mathrm{P}_{(9)}$	922(1)	2847(1)	460(1)	24(1)
$\mathrm{O}_{(1)}$	-2248(2)	4767(1)	2635(1)	30(1)
$\mathrm{O}_{(7)}$	1020(2)	3206(1)	4346(1)	45(1)
$\mathrm{N}_{(3)}$	213(2)	3378(1)	2757(1)	29(1)
$\mathrm{N}_{(8)}$	-693(2)	3761(1)	1147(1)	27(1)
$\mathrm{N}_{(37)}$	5855(4)	391(3)	2734(3)	113(2)
$\mathrm{C}_{(2)}$	–830(2)	3923(1)	2197(1)	26(1)
$\mathrm{C}_{(4)}$	-6(2)	3681(2)	3830(1)	31(1)
$\mathrm{C}_{(5)}$	-1482(2)	4577(2)	4308(1)	34(1)
$\mathrm{C}_{(6)}$	-2541(2)	5079(2)	3713(1)	29(1)
$\mathrm{C}_{(10)}$	1142(2)	1427(2)	804(1)	27(1)
$\mathrm{C}_{(11)}$	-214(2)	1180(2)	1316(2)	36(1)
$\mathrm{C}_{(12)}$	-98(3)	92(2)	1553(2)	44(1)
$\mathrm{C}_{(13)}$	1365(3)	-760(2)	1283(2)	46(1)
$\mathrm{C}_{(14)}$	2720(3)	-524(2)	762(2)	49(1)
$\mathrm{C}_{(15)}$	2612(20)	567(2)	530(2)	41(1)
$\mathrm{C}_{(16)}$	2825(2)	3052(1)	484(1)	25(1)
$\mathrm{C}_{(17)}$	3562(2)	3529(2)	-382(2)	31(1)
$\mathrm{C}_{(18)}$	5000(3)	3699(2)	-346(2)	28(1)
$\mathrm{C}_{(19)}$	5721(3)	3407(2)	527(2)	39(1)
$\mathrm{C}_{(20)}$	5000(3)	2932(2)	1379(2)	42(1)
$\mathrm{C}_{(21)}$	3572(2)	2744(2)	1349(2)	35(1)
$\mathrm{C}_{(22)}$	650(2)	2975(2)	-905(1)	26(10)
$\mathrm{C}_{(23)}$	1724(3)	2202(2)	-1722(2)	35(1)
$\mathrm{C}_{(24)}$	1546(3)	2333(2)	-2778(2)	43(1)
$\mathrm{C}_{(25)}$	315(3)	3212(2)	-3028(2)	44(1)
$\mathrm{C}_{(26)}$	–761(3)	3974(2)	-2221(2)	40(1)
$\mathrm{C}_{(27)}$	-594(2)	3858(2)	-1157(2)	30(1)
$\mathrm{C}_{(28)}$	-4091(2)	5987(2)	4071(2)	32(1)
$\mathrm{C}_{(29)}$	-4415(3)	6580(2)	5053(2)	51(1)
$\mathrm{C}_{(30)}$	-5891(3)	7419(2)	5400(2)	58(1)
$\mathrm{C}_{(31)}$	-7053(3)	7685(2)	4796(2)	46(1)
$\mathrm{C}_{(32)}$	-6709(3)	7110(2)	3811(2)	53(1)
$\mathrm{C}_{(33)}$	-5243(3)	6261(2)	3450(2)	46(1)
$\mathrm{C}_{(34)}$	-8666(3)	8576(2)	5211(3)	67(1)
$\mathrm{C}_{(35)}$	2939(5)	558(4)	3574(5)	109(2)
$\mathrm{C}_{(36)}$	4610(4)	456(2)	3135(3)	73(1)

The 2p_y-AO of the $\mathrm{C}_{(1)}$ atom of the aroylketene molecule **2** and the 2s-AO of the nitrile nitrogen atom of the cyanoimine participate in formation of the $\mathrm{N}_{(3)}$–$\mathrm{C}_{(4)}$ bond. This is supported by the insignificant change in the C≡N bond length in the dienophile compared with the isolated molecule. Participation of the 2p_z- or 2p_y-AOs of the nitrogen in formation of the $\mathrm{N}_{(3)}$–$\mathrm{C}_{(4)}$ bond should have led to a larger increase in the C≡N bond length in the cyano moiety of the activated complexes. The $\mathrm{O}_{(1)}$–$\mathrm{C}_{(2)}$ bond is formed by the orbital in which one of the unshared electron pairs of the oxygen atom is localized and by the 2p_y-AO of the carbon atom.

The calculated enthalpies of formation (ΔH_f) of the activated complexes **A1a** and **A1b** respectively are equal to 471.1 and 431.9 kJ/mol. If we assume that before the reaction the distance between the reagents is infinite and the ΔH_f for such a supermolecule is equal to the sum of the corresponding ΔH_f (**2**+**3**) values, we can estimate the activation energy (E_{act}) as the difference ΔH_f (**A1**) – ΔH_f (**2**+**3**). The value calculated in this way for the reaction **A2a** + **3** is E_{act} = 4.8 kJ/mol, while for **A2b** + **3** it is 5.7 kJ/mol.

TABLE 4. Basic Bond Lengths (*d*) and Bond Angles (ω) in the **5b** Molecule, Calculated by the MNDO, AM1, and MNDO-PM3 Semiempirical Methods

Bond	*d*, Å			Angle	ω, deg.		
	MNDO	AM1	MNDO-PM3		MNDO	AM1	MNDO-PM3
$O_{(1)}-C_{(2)}$	1.372	1.441	1.376	$O_{(1)}-C_{(2)}-N_{(3)}$	124.2	123.5	126.2
$C_{(2)}-N_{(3)}$	1.333	1.337	1.341	$C_{(2)}-N_{(3)}-C_{(4)}$	119.9	119.7	118.3
$N_{(3)}-C_{(4)}$	1.409	1.397	1.424	$N_{(3)}-C_{(4)}-C_{(5)}$	116.3	117.9	116.6
$C_{(4)}-C_{(5)}$	1.491	1.480	1.476	$C_{(4)}-C_{(5)}-C_{(6)}$	119.5	119.6	119.9
$C_{(5)}-C_{(6)}$	1.364	1.352	1.352	$C_{(5)}-C_{(6)}-O_{(1)}$	121.1	122.2	122.4
$C_{(6)}-O_{(1)}$	1.370	1.380	1.381	$C_{(6)}-O_{(1)}-C_{(2)}$	119.0	116.9	116.6
$C_{(4)}=O_{(7)}$	1.230	1.247	1.220	$O_{(1)}-C_{(2)}-N_{(8)}$	110.6	108.9	106.5
$C_{(2)}-N_{(8)}$	1.357	1.303	1.352	$N_{(3)}-C_{(2)}-N_{(8)}$	125.2	127.5	127.3
$N_{(8)}=P_{(9)}$	1.658	1.477	1.675	$C_{(2)}-N_{(8)}=P_{(9)}$	120.5	162.6	125.2
$P-C(Ph_1)$	1.766	1.623	1.803	$N_{(3)}-C_{(4)}=O_{(7)}$	119.1	121.1	118.6
$P-C(Ph_2)$	1.763	1.624	1.793	$C_{(5)}-C_{(4)}=O_{(7)}$	124.6	120.1	124.8
$P-C(Ph_3)$	1.765	1.627	1.793	$N_{(8)}=P_{(9)}-C_{(10)}(Ph_1)$	110.0	111.8	114.0
				$N_{(8)}=P_{(9)}-C_{(16)}(Ph_2)$	115.9	112.9	115.7
				$N_{(8)}=P_{(9)}-C_{(22)}(Ph_3)$	103.9	112.7	106.0

With the aim of determining the reasons for the passivity of compound **3** in the Staudinger type reaction with furandiones **1**, we modeled their [2+2] cycloaddition. For comparison, analogous calculations were performed for furandione **1b** and imine **8**. We found that for the latter reaction we have E_{act} = 63.0 kJ/mol, while for the reaction **1b** + **3** we have 71.9 kJ/mol. According to the calculations, the processes can occur in a concerted fashion, but formation of C–N bonds should be faster than formation of P–O bonds. The transition state for the reaction **1b** + **3** is delayed, i.e., it begins to form at shorter interatomic distances $l_{C \cdots N}$ = 1.674 Å and $l_{P \cdots O}$ = 2.959 Å. For comparison, the corresponding values for the activated complex for the reaction **1b** + **8** are equal to 1.846 Å and 3.199 Å.

TABLE 5. Basic Bond Lengths (*d*), Bond Angles (ω), and Dihedral Angles (θ) in Activated Complexes for Reactions of Benzoyl and *p*-Toluoylketenes with N-cyanotriphenylphosphinimine, Calculated by the MNDO-PM3 Method

Bond	*d*, Å		Angle	ω, deg.		Angle	θ, deg.	
	A1a	**A1b**		**A1a**	**A1b**		**A1a**	**A1b**
$O_{(1)}-C_{(2)}$	2.037	2.038	$O_{(1)}-C_{(2)}-N_{(3)}$	103.5	103.4	$O_{(1)}-C_{(2)}-N_{(3)}-C_{(4)}$	11.5	11.6
$C_{(2)}-N_{(3)}$	1.235	1.235	$C_{(2)}-N_{(3)}-C_{(4)}$	134.2	134.2	$C_{(2)}-N_{(3)}-C_{(4)}-C_{(5)}$	-12.2	-12.3
$N_{(3)}-C_{(4)}$	1.469	1.469	$N_{(3)}-C_{(4)}-C_{(5)}$	117.6	117.6	$N_{(3)}-C_{(4)}-C_{(5)}-C_{(6)}$	3.1	3.2
$C_{(4)}-C_{(5)}$	1.428	1.428	$C_{(4)}-C_{(5)}-C_{(6)}$	124.0	124.0	$C_{(4)}-C_{(4)}-C_{(6)}-O_{(1)}$	1.6	1.7
$C_{(5)}-C_{(6)}$	1.391	1.392	$C_{(5)}-C_{(6)}-O_{(1)}$	123.7	123.7	$C_{(5)}-C_{(6)}-O_{(1)}-C_{(2)}$	-0.8	-1.0
$C_{(6)}-O_{(1)}$	1.277	1.277	$C_{(6)}-O_{(1)}-C_{(2)}$	116.2	116.2	$C_{(6)}-O_{(1)}-C_{(2)}-N_{(3)}$	-4.9	-4.8
$C_{(4)}=O_{(7)}$	1.218	1.218	$N_{(3)}-C_{(4)}=O_{(7)}$	113.0	113.0	$C_{(2)}-N_{(3)}-C_{(4)}=O_{(7)}$	168.7	168.6
			$C_{(5)}-C_{(4)}=O_{(7)}$	129.5	129.5	$N_{(8)}-C_{(2)}-N_{(3)}-C_{(4)}$	-159.0	-159.0
$C_{(2)}-N_{(8)}$	1.303	1.303						
$N_{(8)}=P_{(9)}$	1.685	1.685	$N_{(3)}-C_{(2)}-N_{(8)}$	151.4	151.4	$P_{(9)}=N_{(8)}-C_{(2)}-O_{(1)}$	61.7	61.2
			$C_{(2)}-N_{(8)}=P_{(9)}$	129.9	129.9			

We do not rule out the possibility that the first step of the Staudinger type reaction between furandiones **1** and phosphinimine **3** is irreversible, while elimination of the triphenylphosphine oxide from the [2+2] cycloadducts **6a,b** requires significant consumption of energy. Thermal decarbonylation of the furandiones occurs irreversibly; the reaction of aroyl ketenes **2a,b** and compound **3** is characterized by a low activation barrier, which also determines formation of the phosphorylated 1,3-oxazines **5**.

EXPERIMENTAL

The X-ray diffraction experiment was carried out at -80°C on a Syntex $P2_1$ automatic 4-circle diffractometer (MoKα radiation, graphite monochromator, θ/2θ scanning). The crystals were triclinic, and at -80°C: $a = 8.985(4)$, $b = 12.659(4)$, $c = 12.706(3)$ Å; $\alpha = 89.85(2)$, $\beta = 71.07(3)$, $\gamma = 71.07°$; $V = 1337(1)$ Å^3; $Z = 2$; space group $P1$. Of the total 7259 measured reflections, in further calculations we used 5559 independent observed reflections with $I \geq 2\sigma(I)$. The structure was deciphered by the direct method and refined in the full-matrix anisotropic approximation (in the isotropic approximation for the hydrogen atoms). The final values were $R = 0.049$, $R_w = 0.049$, $GOF = 1.87$. All the calculations were carried out on an IBM PC/AT personal computer using the SHELXTL PLUS software package.

The quantum-chemical calculations were carried out on a Pentium 200 MMX computer using the MOPAC 7.0 software package [13].

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