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Photocyclization of a Mixed Phosphonium–Iodonium Ylide with Phenylacetylene: A Formal Kinetic Approach to the Mechanistic Study

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Abstract—The recently discovered photoheterocyclization of a mixture of mixed phosphonium–iodonium ylides and acetylene compounds to give λ^5-phosphinoline, a new phosphorus-containing heterocycle, occurs with self-acceleration and an induction period at relatively high concentrations of the reactants. The reaction was found to be catalyzed by the acid formed during photolysis. We developed a spectrophotometric method to study the kinetics of photocyclization between phenylacetylene and a phosphonium–iodonium ylide in the presence of trifluoroacetic acid and studied how the yield of target λ^5-phosphinoline and kinetic parameters of the reaction, such as the induction period and maximum rate of product formation, depend on the initial concentrations of the starting compounds and catalyst. It was shown that the addition of the acid has no effect on the critical character of the dependence of the reaction on the concentration of the starting compound: the reaction proceeds only at an ylide concentration of >0.02 mol/L in a microheterogeneous suspension and the self-accelerating character of λ^5-phosphinoline formation is preserved. The optimum reagent ratios maximizing the yield of the target product were determined. The acid was found to play a dual role: it catalyzes the reaction only at concentrations not higher than the initial ylide concentration. At higher acid concentrations, no formation of λ^5-phosphinoline was observed.

Keywords: phosphonium–iodonium ylides, λ^5-phosphinoline, photoheterocyclization, phenylacetylene, acid catalysis

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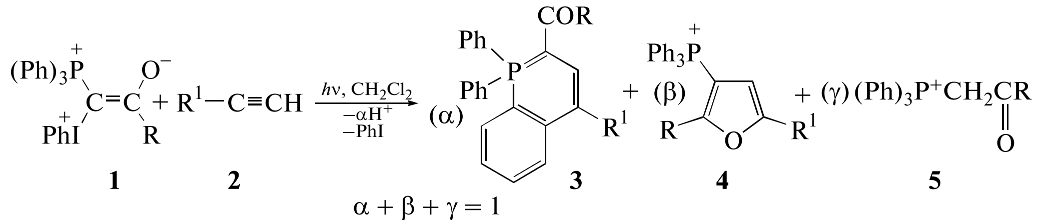
The synthesis and structural and reactivity studies of mixed phosphonium–iodonium ylides allowed design of new reactants for organic synthesis based on these ylides. This class of compounds with several reaction sites opens up new routes to difficult-to-synthesize and new heterocyclic compounds [1–3]. In thermal reactions, mixed phosphonium–iodonium ylides exhibit the properties of alkenyliodonium salts and phosphorus ylides. Mixed ylides (tetrafluoroborates and tosylates) do not enter into the Wittig reaction with different aldehydes [4]. The presence of a very good nucleofuge, viz., the phenyliodonium group, allowed design of processes in which these ylides not only are substrates in nucleophilic substitution but also act as O-nucleophiles [1–3].

The phenyliodonium group as a part of mixed ylides determines their ability to photodecomposition on exposure to light to form reactive ionic and radical ion intermediates, as it was observed for diaryliodonium salts [5, 6]. In recent years, two new photochemical reactions of mixed phosphonium–iodonium ylides with compounds containing a triple bond have been discovered, which yield pseudocycloaddition or heterocyclization products, viz., phosphorus-containing heterocyclic compounds [7–11]. The composition of the products depends on the nature of the triple bond. The photolysis of phosphonium–iodonium ylides in the presence of nitriles RCN affords phosphonium-substituted oxazoles (key precursors in the synthesis of bioactive compounds) in high yields, PhI being a leaving group [7, 11]. The photolysis of a mixture of phosphonium–iodonium ylides (**1**) and acetylenes (**2**) yields several products: λ^5-phosphinolines (**3**), phosphonium-substituted furans (**4**), PhI, and phosphonium salts (**5**) (Scheme 1, the BF_4^- counter ion is omitted) [9, 10, 12]. The relative yields of products **3**–**5** depend significantly on the acetylene structure [10].

An analysis of Scheme 1 [12] demonstrated the following features of the reaction: firstly, reaction products **3**–**5** contain no iodine, which is released as phenyl iodide; secondly, λ^5-phosphinoline is a neutral compound whose formation from the ylide (cation) and acetylene is accompanied by proton elimination, i.e., the formation of acid with counterion (BF_4^-);



Scheme 1.

thirdly, the formation of phosphonium salt **5** requires two additional hydrogen atoms (CH_2 group of the salt). While the formation of furan derivative **4** can be assumed to be analogous to the formation of oxazoles upon the photolysis of **1** in solutions of nitriles [7, 11], the mechanism of λ^5-phosphinoline formation, a quite unusual heterocycle, has not been clarified completely. To date, a great number of substituted λ^5-phosphinolines have been synthesized from ylides with different substituents at the double bond and heteroaryl substituents at the phosphorus atom using acetylenes with different structures [13–15]. In some cases, the corresponding λ^5-phosphinoline is the main photolysis product (for example, for phenylacetylene the yield of **3** is 60% and the yield of **4** is less than 7% [9]). Note that the formation of λ^5-phosphinoline occurs in a one-pot metal-free system at room temperature within less than 30 min, which is not quite common for organic synthesis reactions.

As was noted earlier [12], the formation of λ^5-phosphinoline has some specific features that are not typical of homogeneous organic reactions. It was established that the reaction between **1** (R = Ph) and **2** (R^1 = Ph) yielding **3** occurs only at relatively high concentrations of **1** (≥0.02 mol/L in CH_2Cl_2). At these concentrations, ylide **1** is not soluble completely in CH_2Cl_2 and produces a weakly opalescent suspension. The solution is light yellow, whereas the starting ylide **1** in the crystalline state is a white powder. The reaction is initiated by light with a wavelength of 350–450 nm, a range in which ylide **1** does not noticeably absorb light at concentrations of 10^{-4} mol/L, which are commonly used in spectrophotometric measurements. However, when the concentration of **1** is higher or a cell with an optical path length of 5 cm is used, the “tail” of UV absorption is observed in the visible region up to 460 nm. The development of the reaction is unusual. An induction period is observed during which there are no changes in the visible absorption spectrum at the wavelengths at which λ^5-phosphinoline **3** absorbs (Fig. 1). Thereafter, the reaction develops spontaneously, starting locally either on heterogeneous particles of ylide **1** or on the cell wall or at the solution surface, and this is manifested as the appearance of a bright-brown spot. Within 1–2 min, the reaction propagates throughout the bulk of the solution and stops. The final solution is brown and transparent. The visible absorption spectrum of the colored product corresponds to that of λ^5-phosphinoline **3**.

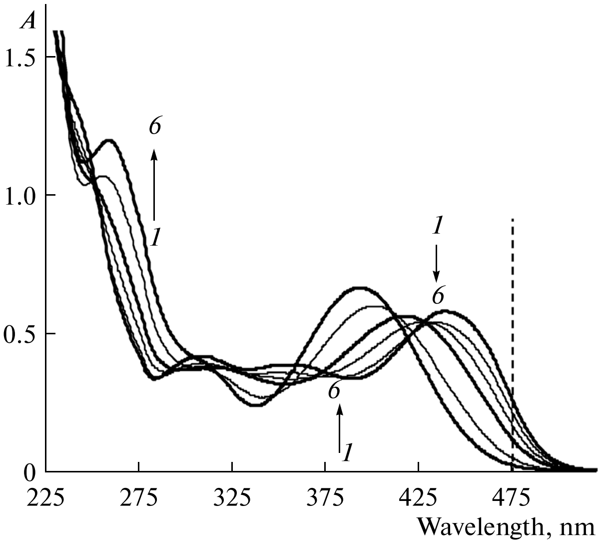


Fig. 1. Absorption spectrum of λ^5-phosphinoline as a function of the TFA concentration, 10^4 mol/L: (*1*) 0, (*2*) 0.55, (*3*) 1.13, (*4*) 2.4, (*5*) 6.0, and (*6*) 12.0. The solvent is CH_2Cl_2, l = 0.4 cm. The dashed line indicates the registration wavelength in the kinetic experiments.

The development of the reaction suggests that it occurs via a autocatalytic or chain mechanism, and the principal question arising here concerns the nature of the products ensuring autocatalysis or chain propagation and branching. The above-noted acid formation that follows from the reaction stoichiometry (Scheme 1) is confirmed by a comparison between the pH values of aqueous extracts of the starting and final solutions, which indicates a noticeable increase in the acidity of the reaction mixture during the reaction (pH 6.0 and pH 2.0, respectively). It was assumed [12] that the acid released initiates the photodecomposition of the ylide and, upon photoinitiation in the close proximity of a heterogeneous particle, where the local concentrations of the reagents are higher, due to the photodecomposition of the ylide the acid concentration reaches the critical value necessary for acid catalysis before it reaches the same value in the solution bulk. This initiates a spontaneous development of the acid-catalyzed process and its propagation throughout the bulk of the mixture. Thus, light acts as an initiator triggering the self-catalyzed process. Preliminary experiments have shown that the addition of strong organic acids (trifluoroacetic acid, *p*-toluenesulfonic acid, as well as HBF_4) shortens the induction time and accelerates the reaction [12]. The addition of weak acetic acid has no effect on the course of the reaction.

Thus, the process under study is an example of reaction that can be regarded as a photoinitiated reaction catalyzed by one of the final products, viz., an acid. The kinetics of this reaction under steady-state photolysis conditions is difficult to study, since the reaction proceeds at high concentrations of the starting compound, at which a direct spectrophotometric study is impossible and, therefore, the samples must be diluted 50- to 100-fold for making a spectrophotometric analysis. One should take into account that slight stirring of the mixture disturbs the course of the process by changing the local concentrations of the reactants. Finally, after the end of the induction period, the reaction develops very rapidly (within 2–3 min) and, under these conditions, it is difficult to take a sufficient number of samples for kinetic measurements. The possibility of the photochemical reaction turning into an acid-catalyzed one allowed us to study the formal kinetics of λ^5-phosphinoline formation in the reaction between ylide **1** and phenylacetylene **2** and to determine some kinetic parameters of the reaction and the critical concentrations of the reactants. This can provide a key to determining the optimum conditions for the preparation of λ^5-phosphinoline in the course of the complex photocatalytic process.

EXPERIMENTAL

Ylide **1** (R = Ph) was synthesized according to the procedure described in [1, 8, 9].

The reaction between ylide **1** (R = Ph) and phenylacetylene **2** in the presence of trifluoroacetic acid (TFA), which was found to be most convenient from the experimental standpoint, was studied in the cell compartment of a UV-3101 PC spectrophotometer (Shimadzu, Japan) by monitoring the formation of the colored reaction product, λ^5-phosphinoline (**3**), at 475 nm in the kinetic mode. As was noted above, in steady-state photolysis, the reaction proceeds only at sufficiently high concentrations of the starting compounds (>0.02 mol/L); for this reason, the formation of the final colored product was monitored on the long-wavelength absorption wing of compound **3** using a cell with an optical path length of 0.4 cm (Fig. 1). A weighed portion of the ylide was dissolved in CH_2Cl_2 using an ultrasonic bath. The solution with an ylide concentration above 0.02 mol/L was actually a light yellow, weakly opalescent suspension. The experiment was performed as follows: to a solution of ylide **1** in CH_2Cl_2 (0.01–0.12 mol/L, 1.5 mL), phenylacetylene was added using a micropipette so that its concentration was equal to, or 2–10 times higher than, the concentration of **1**. The resulting solution was poured into a quartz cell with an optical path length of 0.4 cm and was placed into the cell compartment of the spectrophotometer, an appropriate amount of a TFA solution in CH_2Cl_2 (0.2 mL of TFA in 2 mL of CH_2Cl_2, $[TFA]_0 = 1.35$ mol/L) was added using a micropipette, and monitoring the formation kinetics of the colored product (475 nm) was begun. The concentration of the acid was varied in the 0.009–0.675 mol/L range. A comparison between the formation kinetics of compound **3** in the presence of atmospheric oxygen and after purging the mixture with an inert gas indicated no effect of oxygen on the reaction, and, for this reason, the reaction was performed in air. We studied how the induction period of compound **3** formation and the maximum rate of the process after the end of the induction period depend on the initial concentrations of ylide, phenylacetylene, and added acid. The change in absorbance per unit time (dA/dt) at the measurement wavelength (475 nm) was taken to be the reaction rate.

The solution of ylide in CH_2Cl_2 was observed to undergo changes when it was left to stand even for a short time (30 min). In particular, it was shown that the ylide particles undergo aggregation, which affects the induction time and the process rate, but not the yield of the final product. For this reason, a new ylide sample was used in each experiment, and it was dissolved in CH_2Cl_2 immediately before the experiment. Due to the slight quantitative discrepancy between the results obtained using different batches of ylide, which could contain trace amounts of an acid, the quantitative parameters given in the table for different reaction conditions refer to certain experimental series, each performed for 1 day with the same batches of ylide and solvent. It should be noted that, regardless of the ylide batch used, all reaction regularities are qualitatively reproduced.

When the reaction was complete, the final solution was diluted 50- to 100-fold with CH_2Cl_2 and the absorption spectrum was recorded on a UV-3101 PC spectrophotometer, from which the final concentration of compound **3** and its yield were calculated. As follows from Fig. 1, compound **3** has two protonated forms (the absorption maxima at 439, 418, and 391 nm correspond to the neutral and protonated forms, respectively) with similar absorption coefficients ($\sim 1.25 \times 10^4$ L mol^{-1} cm^{-1}). Upon dilution with CH_2Cl_2, the spectrum of the product corresponded to the protonated form with the absorption maximum at ~400 nm (Fig. 1).

RESULTS

Kinetic Parameters of the Reaction as a Function of the Concentration of Mixed Ylide and Phenylacetylene

Earlier, it was shown that the formation of compound **3** upon steady-state photolysis in the absence of an acid occurs at a ylide **1** concentration above

Induction time, maximum rate, and λ^5-phosphinoline (**3**) yield in relation to the initial concentrations of ylide **1**, phenylacetylene **2**, and trifluoroacetic acid

Series	$[\mathbf{1}]_0$,	$[\mathbf{2}]_0$,	$[\mathrm{TFA}]_0$,	t_{ind}, s	$w_{\max}$*, s^{-1}	Yield of **3**, %
	mol/L					
1	0.025	0.075	0	>10000	–	0
	0.0125	0.0375	0.023	>2400	0	0
	0.025	0.075	0.023	388	0.04	32 ± 3
	0.050	0.15	0.023	200	0.15	38 ± 4
	0.10	0.30	0.023	113	0.24	37 ± 4
2**	0.075	0.225	0.023	180	0.07	–
	0.075	0.225	0.046	127	0.11	
	0.075	0.225	0.07	125	0.13	
	0.10	0.30	0.023	150	0.11	
	0.11	0.33	0.023	133	0.13	
	0.12	0.36	0.023	120	0.14	
3	0.025	0.024	0.023	730	0.013	17 ± 2
		0.048		730	0.014	19 ± 2
		0.072		411	0.04	32 ± 3
		0.096		285	0.09	32 ± 3
		0.144		207	0.09	32 ± 3
		0.192		196	0.09	32 ± 3
4	0.025	0.12	0.009	970	0.01	32 ± 3
			0.023	490	0.026	32 ± 3
			0.045	750	0.0014	2 ± 0.5
			0.09	$>10^4$	0	0
			0.18	$>10^4$	0	0
			0.45	20	0.0008	0
			0.54	20	0.0014	0
			0.675	0	0.006	0

* The reaction rate is expressed in terms of a change in absorbance per second.

** In series 2, the yield of **3** was not determined.

0.02 mol/L [12]. Since in the present study the reaction was carried out under different conditions (without using an external source of radiation in the spectrophotometer cell compartment in the presence of acid), we performed series of experiments at different initial concentrations of ylide **1** in the presence of a 3-fold excess of phenylacetylene **2** at an acid concentration of 0.023 mol/L (table, series 1). The experiment carried out in the absence of an acid showed that no formation of colored products occurs upon 3-h-long incubation of a solution of the (**1** + **2**) mixture in the spectrophotometer cell compartment. In the presence of the acid, the reaction pattern changes dramatically (Fig. 2a). At $[\mathbf{1}]_0 \geq 0.025$ mol/L, the formation of **3** is observed after an induction period and, with an increasing $[\mathbf{1}]_0$, the induction time decreases and the reaction rate after the end of the induction period increases (table, series 1 and 2). The yield of the target compound at an ylide concentration of 0.05 mol/L almost reaches the maximum value of ~40% of the ylide added to the reaction (table).

Thus, the lower concentration limit of ylide **1** at which the formation of λ^5-phosphinoline occurs is the same for both the steady-state photolysis conditions and the reaction occurring without external irradiation in the spectrophotometer cell compartment in the presence of the acid. The plot of the maximum rate of the process as a function of the initial concentration of ylide **1** is nearly linear and intersects the x axis at $[\mathbf{1}]_0 =$ 0.016–0.018 mol/L, the point corresponding to the lower limit of reactive ylide concentration. Note that, although a colored product is not produced at ylide concentrations of **1** < 0.02 mol/L, this does not mean that ylide undergoes no conversion under these conditions, since when ylide **1** is exposed to light and acid, it turns slowly into salt **5** and other compounds having no visible absorption. It is important that in this case there are no traces of the photoheterocyclization product **3** (table, series 1, run 2).

A comparison between the induction periods for acid-containing solutions showed that these periods are significantly shorter when the mixture is placed in the spectrophotometer, as well as when it is exposed to

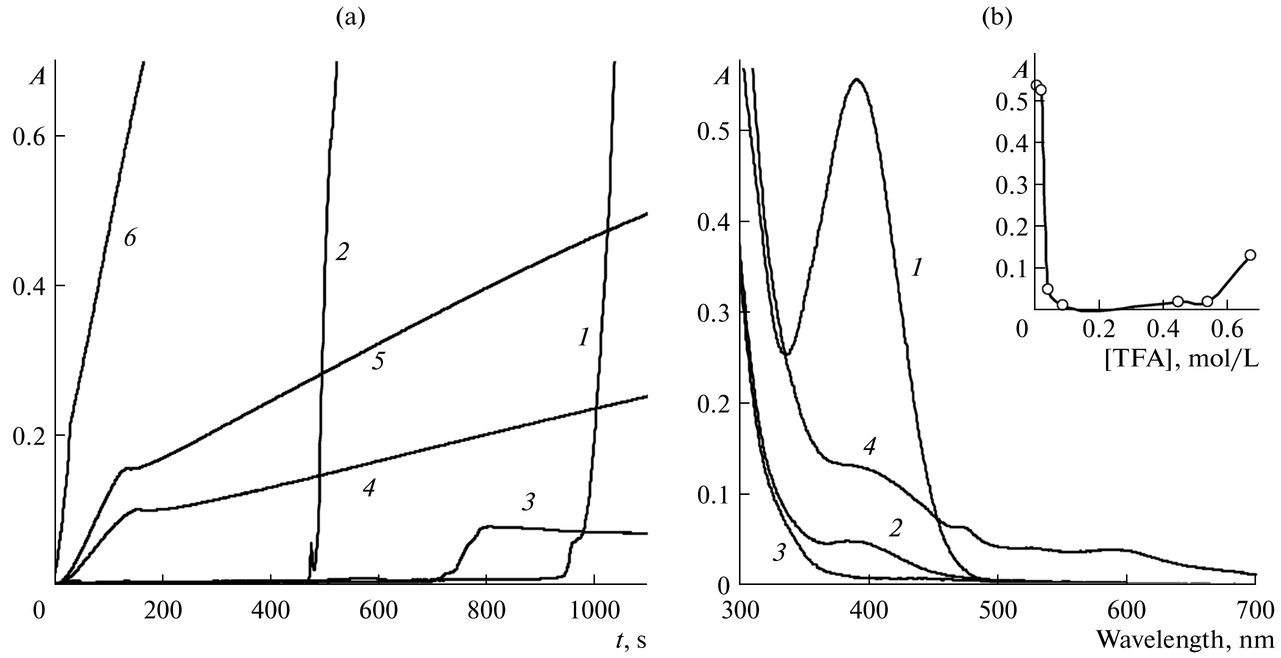


Fig. 2. (a) Kinetics of the formation of the compounds produced in the reaction between **1** (0.025 mol/L) and **2** (0.12 mol/L) in the presence of TFA at concentrations of (*1*) 0.009, (*2*) 0.023, (*3*) 0.045, (*4*) 0.45, (*5*) 0.54, and (*6*) 0.675 mool/L. λ_{req} = 475 nm, CH_2Cl_2. (b). Absorption spectra of the final reaction products at different TFA concentrations, mol/L: (*1*) 0.009, (*2*) 0.045, (*3*) 0.09, and (*4*) 0.675. 1 : 50 dilution with CH_2Cl_2. Inset: absorbance of the final product at 400 nm as a function of the concentration of added acid.

scattered light, than when the solution is stored in the dark. Thus, the low-intensity light of the probing lamp with a wavelength of 475 nm initiates reaction in the presence of the acid but does not initiate the reaction in the absence of an acid. The appearance of small fluctuations in absorbance shortly before the end and simultaneously after of the induction period (Fig. 2a) suggests that the reaction in the spectrophotometer does not start simultaneously in the entire bulk (similarly to the photolysis under external irradiation). This is confirmed by the behavior of the solution that was left in the light: the reaction commences at the surface of the solution

The yield of phosphinoline **3** in the solution incubated in the dark was by 15% less than that in the solution incubated in the spectrophotometer. The spectrum of the product displayed slight absorption at $\lambda \geq$ 500 nm, where phosphinoline **3** does not absorb. The yield of **3** in the case of reaction in the presence of TFA (~40%) was lower than that under the conditions of steady-state photolysis of a neutral solution of the ylide (at most 60%). The causes of this effect will be discussed below.

Kinetic parameters of the formation of **3** as a function of phenylacetylene concentration were studied at constant concentrations of ylide **1** (0.024 mol/L) and TFA (0.023 mol/L) and different concentrations of **2** varying from 0.024 to 0.192 mol/L (table, series 3). The results obtained show that, at the concentration of **2** that is 3 times higher than the concentration of the starting ylide **1**, the reaction yield does not depend on the concentration of **2**. This conclusion was also confirmed at other initial concentrations of the ylide. The induction period of the reaction decreases with an increasing concentration of **2**, and it tends to a limit at sixfold excess of the ylide. The maximum reaction rate after the induction period does not depend on the concentration of **2** at its fourfold excess. Note that at all ylide and phenylacetylene concentrations examined, an induction periods and a subsequent self-accelerated progress of the reaction were observed. Thus, the optimum initial concentration of phenylacetylene is its 3- or 4-fold excess over the ylide concentration.

Kinetic Parameters of the Reaction as a Function of the Concentration of Trifluoroacetic Acid

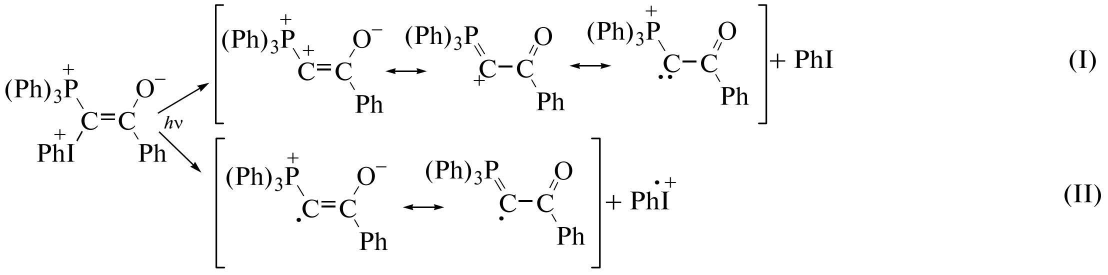
Figure 2a shows the kinetic curves as changes in absorbance at 475 nm in the presence of TFA at different concentrations (table, series 4). Correlating the kinetic data with the analysis of the reaction products (Fig. 2b) shows that a high-yield formation of **3** occurs only at $[TFA]_0 \leq [\mathbf{1}]_0$. As the TFA concentration is further increased, the yield of the target product decreases dramatically and the induction time increases (Fig. 2a, curve 3). At $2[\mathbf{1}]_0 < [TFA]_0 < 15[\mathbf{1}]_0$, colored products does not form at all. At acid concentrations of $[TFA]_0 > 2[\mathbf{1}]_0$, the solution becomes homogeneous and colorless; i.e., the ylide dissolves completely in CH_2Cl_2. A further increase in the TFA concentration ($[\mathrm{TFA}]_0 \geq 15[\mathbf{1}]_0$) results in the formation of colored products virtually without an induction period (Fig. 2a, curves *4–6*). These products absorb in the visible region up to 700 nm with absorbance maxima at 600, 480, and 400 nm (Fig. 2b, curve *4*). Probably, they are oligomeric products of reactions of phenylacetylene with other products of ylide decomposition in the acidic medium. The kinetic curves for the formation of these products have a pronounced break, indicating two steps of the process at high acid concentrations.

The observed dependence of the reaction pathway on the acid concentration was unexpected, and, for this reason, the behavior of ylide **1** in the presence of different concentrations of the acid was studied in greater detail. The experiments were performed at an ylide concentration of 1×10^{-4} mol/L. Up to a twofold excess of the acid, the absorption spectrum of the ylide changed only slightly. At higher concentrations of the acid, the spectrum of the ylide displays significant changes: a new peak with $\lambda_{\max} = 269$ nm appears. At a 20-fold excess of the acid, this peak appears almost immediately after mixing the reagents. At lower concentrations of TFA, the formation of the product corresponding to this peak is complete in 15 min. After the extraction of the acid with water, the spectrum of this product remained unchanged; i.e., the product does not result from the acid–base equilibrium and the reaction of the ylide with excess acid is irreversible. This result suggests that the formation of **3** involves only the starting form of ylide **1**, but not products of its transformation in the acidic medium.

In the experiments at an ylide concentration of 0.075 mol/L, we studied in detail how the induction time and the reaction rate depend on the TFA concentration at $[\mathrm{TFA}]_0 \leq [\mathbf{1}]_0$ (table, series 2). In this case, the induction time decreases with an increasing acid concentration in the $[\mathrm{TFA}]_0 < [\mathbf{1}]_0$ range; however, at $[\mathrm{TFA}]_0$ of 0.046–0.07 mol/L the induction time remains virtually unchanged and the reaction rate increases after the end of the induction time.

DISCUSSION

Photochemical reactions in the ylides under study are caused by the presence of the phenyliodonium fragment. Diaryliodonium salts are widely used as polymerization photoinitiators, and the mechanism of their photodecomposition was comprehensively studied [5, 6]. On being exposed to light, these compounds undergo decomposition both via a heterolytic mechanism as a result of photoinduced electron transfer to form PhI and ionic intermediates and via a homolytic mechanism to form radicals and radical ions. Extension of the decomposition mechanism of diaryliodonium salts to the photodecomposition of the mixed phosphonium–iodonium ylide can be represented as follows:



Scheme 2.

The heterolytic (I) and homolytic (II) photodecomposition of ylide **1** results in the formation of a complex mixture of reactive ionic, radical ion, radical, and, possibly, carbene intermediates that can react with the solvent (CH_2Cl_2) and with the added reagent, for example, phenylacetylene.

The study of the product composition and mechanism of photolysis of mixed ylides with different acetylenes and nitriles showed that the pseudocycloaddition reactions occur with a high probability due to the heterolytic decomposition of ylide in the reaction of the added compound containing a triple bond with an ionic intermediate, and the phosphonium salt and other transformation products of ylide result from transformations of radical intermediates [11, 12]. The fact that photodecomposition of ylides proceeds via two parallel pathways limits the yields of target products. In contrast to pseudocycloaddition, which occurs in a homogeneous solution even at low concentrations of ylides (10^{-4} mol/L), heterocyclization is observed only at ylide concentrations above 0.02 mol/L in a microsuspension in CH_2Cl_2, with the acid released in the reaction playing an important role. Note that the reaction of the solvent with the radical ion $PhI^{\bullet +}$ formed upon the homolytic decomposition of ylide **1** (reaction (II)) also results in the formation of an acid according to reaction (III) [5, 6]:

$$PhI^{\bullet +} + CH_2Cl_2 \rightarrow PhI + H^+ + C^{\bullet}HCl_2. \qquad \text{(III)}$$

Therefore, one can assume that it is via reaction (III) that the acid forms initially upon the steady-state photolysis of the (**1** + **2**) mixture as a result of the homolytic decomposition of the ylide and this acid triggers heterocyclization. To verify this assumption, we performed two experiments. In the first experiment, in the steady-state photolysis of the mixture of **1** (0.05 mol/L) and **2** (0.15 mol/L) the induction period was 4 min (Fig. 3a). In the second experiment, ylide **1** (0.05 mol/L) was photolyzed for 4 min and compound **2** (0.15 mol/L) was then added. The formation of **3** started only 4 min after the addition of **2** (Fig. 3b); i.e., the acid formed in the steady-state photolysis of **1** upon its homolytic decomposition is not accumulated and seems to be consumed in the formation of phosphonium salt, as was suggested in [11, 12].

Thus, it is the mixture of the reagents that creates a medium necessary for the initiation of heterocyclization. This suggests that complexation between **1** and **2** in the heterogeneous system (**1** + **2**) favors the photodecomposition of the ylide via the heterolytic mechanism. Such a complex was actually observed in the reactant mixture by spectrophotometry. The activation of the triple bonds of arylalkynes by iodonium salts forming in situ was assumed, for example, in the organic synthesis of spiro compounds [16]. Apparently, such activation can occur also upon the complexation of a mixed ylide with acetylenes. In this regard, our result on the photoinitiation of the reaction in the presence of TFA by light with a wavelength of 475 nm, at which the ylide absorbance is negligible, is likely explained by the specific photophysical and photochemical properties of the nanoparticles formed by the ylide in its complex with phenylacetylene.

The question now arises of what kinds of chemical processes occur during the induction period. Spectra *1–3* in Fig. 3a clearly show that UV-absorbing products form during the induction period of the (**1** + **2**) mixture. Upon photolysis of the individual ylide, the spectral changes at the same point in time are significantly less (Fig. 3b, spectra *1*, *2*). Unfortunately, the mass spectrometry of the samples taken during the induction period detected no noticeable formation of any unknown products with an ionic mass above 100 Da. The samples taken before the end of the induction period contain, besides ions of the starting compounds, small amounts of ions with masses corresponding to the final products, viz., λ^5-phosphinoline and the phosphonium salt. These data suggest that, although the formation of UV-absorbing intermediates upon the photolysis of the mixture was observed during the induction period, these intermediates, on the one hand, decompose during the mass spectrometric analysis and do not manifest themselves and, on the other hand, result in the formation of the target product and acid.

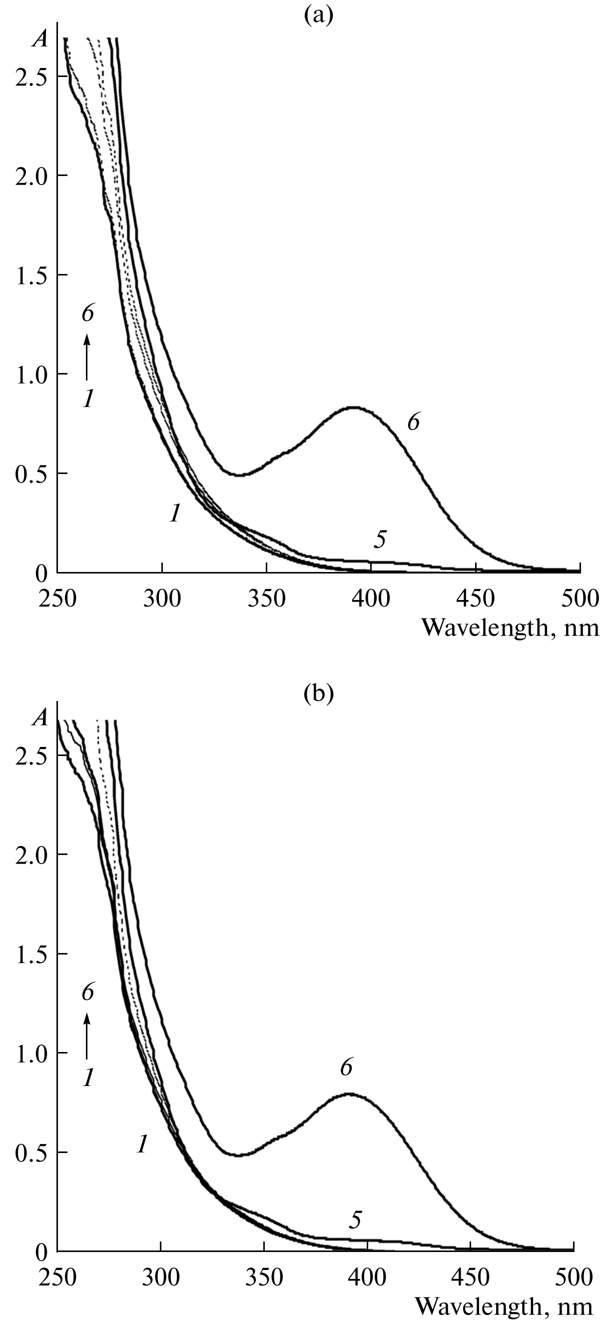


Fig. 3. (a) Evolution of the absorption spectrum in the steady-state photolysis of a mixture of **1** (0.05 mol/L) and **2** (0.15 mol/L); photolysis time, min: (*1*) 0, (*2*) 1, (*3*) 2, (*4*) 3, (*5*) 4, and (*6*) 7. (b) Evolution of the absorption spectrum in the steady-state photolysis of ylide **1** (0.05 mol/L); photolysis time, min: (*1*) 0 and (*2*) 4; after the addition of **2** (0.15 mol/L) for the total photolysis time, min: (*3*) 4, (*4*) 7, (*5*) 8, and (*6*) 10 (*6*). λ_{exc} = 400 nm, 1 : 200 dilution with CH_2Cl_2.

The complicated dependences of the product yield and kinetic parameters of the reaction on the acid concentration are due to the reactions of ylides with excess acid. It should be noted here that, under the steady-state photolysis conditions without the addition of an acid, the concentration of liberated H^+ cannot be higher than the initial ylide concentration; therefore, in this case the acid concentration remains at the optimum level throughout the process. This fact is responsible for the phosphinoline **3** yield in the

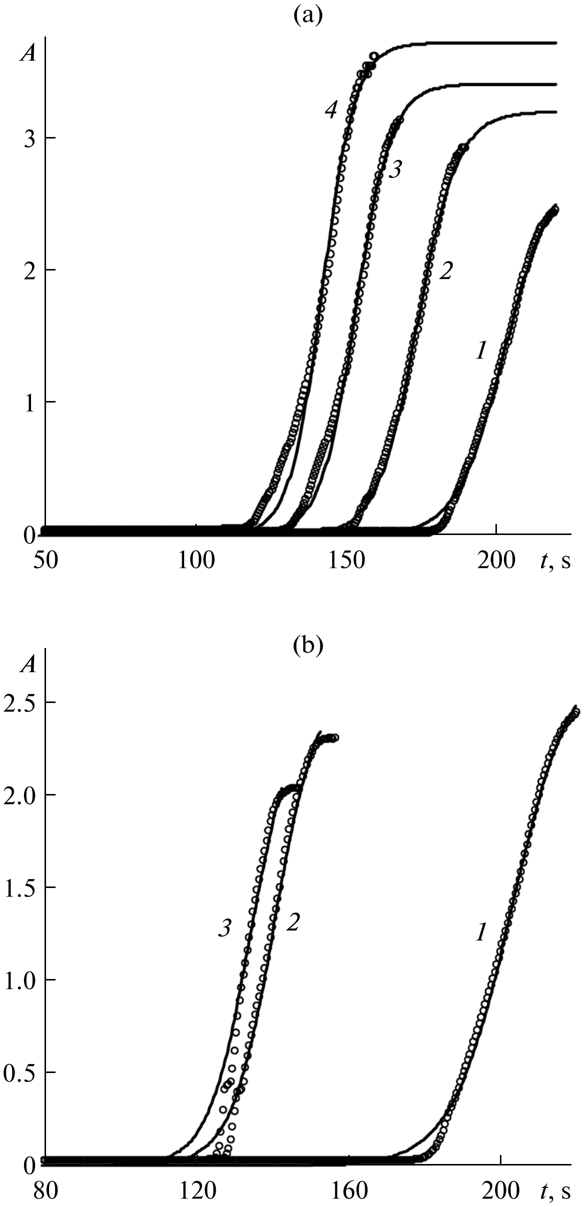


Fig. 4. Experimental kinetic curves for the change in absorbance at 475 nm (points) for (**1** + **2** + TFA) mixtures and their fits to Eq. (1) (solid curves): (a) at different values of $[\mathbf{1}]_0$, mol/L: (*1*) 0.075, (*2*) 0.10, (*3*) 0.11, and (*4*) 0.12, $[\mathrm{TFA}]_0 = 0.023$ mol/L; (b) at different values of $[\mathrm{TFA}]_0$, mol/L: (*1*) 0.023, (*2*) 0.046, and (*3*) 0.07, $[\mathbf{1}]_0 =$ 0.075 mol/L. In all experiments, $[\mathbf{2}]_0 = 3[\mathbf{1}]_0$.

steady-state photolysis being higher than the yield observed upon the addition of the catalyzing acid, since in the latter case the acid concentration during the reaction much earlier begins to exceed the current ylide concentration and the acid converts the ylide into its inactive form.

The formation of phosphinoline **3** is a complex heterogeneous-homogeneous reaction induced by light and catalyzed by H^+ that forms both upon the photodecomposition of the starting phosphonium–iodonium ylide and upon the formation of **3** [5, 6, 12]. The reaction under study proceeds in the phenylacetylene–ylide complex in excess phenylacetylene, and, therefore, in the first approximation it can be regarded as an autocatalytic first-order reaction catalyzed by the final product rather than the target product.

To fit experimental data, we used the equation describing an autocatalytic first-order reaction [17]. The value measured here is the absorbance due to product **3**. All remaining components of the mixture, including the initiating admixture of TFA, show no noticeable absorbance in the visible region, so the equation for the autocatalytic reaction was used in the following form:

$$A = \frac{[\mathrm{H}^+]_0[\mathbf{1}]_0(\exp(k([\mathbf{1}]_0 + [\mathrm{H}^+]_0)t) - 1)}{[\mathbf{1}]_0 + [\mathrm{H}^+]_0\exp(k([\mathbf{1}]_0 + [\mathrm{H}^+]_0)t)}\gamma, \qquad (1)$$

where A is the current absorbance of phosphinoline **3** at the registration wavelength (475 nm), $[\mathbf{1}]_0$ and $[\mathrm{H}^+]_0$ are the initial concentrations of ylide and catalyzing admixture, respectively, k is the rate constant of the second-order reaction (L mol^{-1} s^{-1}), t is time (s), and γ is the factor converting the concentration of **3** into the measured absorbance, which is determined by the molar absorption coefficient of **3** at the registration wavelength (475 nm), optical path length (0.4 cm), and an additional factor accounting for the fact that the target product yield is significantly lower than 100% (in L/mol). To estimate the rate constant, the experimental curves obtained in series 2 were fitted to Eq. (1).

Assuming that $[\mathrm{H}^+] = [\mathrm{TFA}] = 0.023$ mol/L, it is impossible to describe the formation kinetics of **3** at varied concentrations of ylide **1** (series 2), since a high concentration of the catalyzing admixture results in the absence of an induction period. However, the calculated curves adequately reflect the formation regularities of **3** under variations of both the ylide concentration at [TFA] = 0.023 mol/L (Fig. 4a) and the TFA concentration from 0.023 to 0.07 mol/L and at a constant ylide concentration (Fig. 4b) at a concentration of catalyzing additive $[\mathrm{H}^+]$ of about 10^{-12}–10^{-13} mol/L. At a constant acid concentration of $[\mathrm{H}^+] = 5.4 \times 10^{-13}$ mol/L, regardless of the initial ylide concentration, we obtained close values of the rate constant $k = (1.57 \pm 0.15)$ L mol^{-1} s^{-1} and $\gamma =$ (35 ± 3) L/mol. By fitting the kinetic curves at different TFA concentrations and constant concentration of $[\mathbf{1}] = 0.075$ mol/L (Fig. 4b), the following values were obtained: $[\mathrm{H}^+] = 5.4 \times 10^{-13}$, 10.8×10^{-13}, and 16.2×10^{-13} mol/L and $k = 1.68$, 2.35, and 2.45 L mol^{-1} s^{-1} at [TFA] = 0.023, 0.046, and 0.07 mol/L, respectively. The ten-orders difference between the concentration of the added acid and the calculated concentration of catalyzing additiveH^+ is caused by several factors and reflects, first of all, the low degree of dissociation of the acid in the nonpolar organic solvent. Note that the estimate of the parameter γ does not contradict the experimental values of molar absorption coeffiicient and reaction yield.

The runs of the calculated curves coincide incompletely with the experimental dependences, which is undoubtedly due to the simplified character of the model applied. In the experiment at all concentrations of the ylide and acid, a steeper beginning and end of the reaction were observed. The former is due to the heterogeneous character of the reaction, and the latter is due to the accumulation of the acid, which transforms the ylide into its inactive form. It is interesting that at high concentrations of the ylide (>0.1 mol/L, Fig. 4a, curves *3*, *4*), the initial reaction rates after the end of the induction period virtually do not depend on the ylide concentration. This is likely caused by the large size of the ylide particles at these concentrations, which result in the absence of a dependence of the reaction rate on the ylide concentration at the initial stage. In the developed reaction at a higher concentration of the ylide, the maximum reaction rate is higher in both the experiment (table) and calculations.

The results obtained emphasize once again the complex mechanism of the reaction, which cannot be described completely by the simplified model. The dependence of the rate constant k on the acid concentration possibly means that, during the formation of **3**, the acid is not only involved in the initiation of the reaction, but it also carries out the acid catalysis in transformations of intermediates in the formation of the target product. One cannot exclude also that the increase in the acid concentration results in the formation of one more species catalyzing the reaction.

In conclusion, it should be emphasized that this experimental spectrophotometric and formal kinetic studies of the complex photochemical synthesis of λ^5-phosphinoline under conditions of pure photochemical initiation changing to initiation in the presence of acid allowed determination of the optimum ratios of the reagents maximizing the yield of the target product. The kinetic parameters of the process were found to depend on the concentration of the added acid in a complex manner. This study raised a set of questions that cannot be answered within a formalized kinetic approach and require studying the mechanism of photoinitiation in the presence and in the absence of an acid, the role of heterogeneous state of the starting ylide, and the effect of particle size on the course of the reaction. A detailed spectral kinetic analysis of reactive intermediate species (ions and radicals) using pulse methods and EPR spectroscopy would allow determination of their roles in the formation of final products.

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