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Mechanism and Remarkable Features of Photoinduced Cycloaddition of Phenylacetylene to Mixed Phosphonium–Iodonium Ylide

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In recent years, the investigation of the structure and reactivity of an almost uninvestigated class of mixed phosphonium—iodonium ylides allowed us to create novel reagents for organic synthesis on their basis. This class of compounds with several reactive centers exhibits new reactions and opens new routes to the synthesis of not easily accessible and novel heterocyclic compounds [1–3]. Recently, we described two unknown photochemical reactions of mixed phosphonium—iodonium ylides in the presence of compounds with triple bond to give products of pseudo-cycloaddition [4–7]. The direction of the photolysis depends on the structures of the compounds with a triple bond. Nitriles R₁CN afford oxazoles with high yield, PhI being the leaving group [4]. When the reaction occurs between mixed phosphonium–iodonium ylide (1) and acetylenes (2), λ^5 -phosphinoline (4), furan derivative (5), PhI (3), and phosphonium salt (6) are formed as a

result of the photolysis (Scheme 1; the counterion BF_4^- is omitted in Scheme 1 and further on for simplicity) [6, 7]. The relative yield of products **4**–**6** depends substantially on the structure of acetylene [7].



where α , β , γ is the relative yield of products.

Scheme 1.

From examination of Scheme 1, the following points should be emphasized: (1) all reaction products do not contain iodine, which is evolved in the form of iodobenzene **3** in the amount equimolar to ylide **1** consumed; (2) λ^5 -phosphinoline is a neutral com-

pound and its formation from ylide 1 (the cation!) is accompanied by elimination of proton; and (3) two extra hydrogen atoms are necessary for the formation of phosphonium salt **6** (the CH_2 group of the salt).

The mechanism of the formation of the furan derivative **5** is probably similar to that of the oxazole formation in the photolysis of **1** in the solutions of nitriles [4, 5], whereas the regularities of the formation of λ^5 -phosphinoline, a relatively exotic heterocycle, deserve special attention. This is particularly necessary to take into account because sometimes, for example, in the reaction of **1** (R¹ = Ph), we omit the designation of this group further on) with phenylacetylene **2** (R² = Ph), the corresponding λ^5 -phosphinoline is a major prod-

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Fig. 1. Development of the reaction between ylide 1 and phenylacetylene 2 in CH₂Cl₂ upon irradiation by the light with λ_{irr} 400 nm. Irradiation time, min: (1) 0, (2) 7.0, (3) 7.25, (4) 7.5, (5) 7.75, (6) 8.00, (7) 8.5 and (8) 9.0.

uct of the photolysis (the yields of **4** and **5** are 60%, and less than 7%, respectively [6]).

In this communication, we present the more detailed study of the reaction between 1 and 2 in the CH₂Cl₂ solution carried out by steady-state photolysis. It has been found that the reaction between 1 and 2 to give 4 occurs only at relatively high concentrations of 1 (0.02 mol L^{-1} and more in CH_2Cl_2). At these concentrations, ylide 1 is not completely soluble in CH₂Cl₂ and gives weakly opalescent suspension. The solution is light yellow, whereas the parent ylide 1 in crystalline form is white powder. The reaction was carried out at a fivefold excess of acetylene 2 and was induced by irradiation with the light with λ from 350 to 450 nm, where ylide 1 in concentrations usually used in the spectrophotometric measurements ($10^{-4} \text{ mol } L^{-1}$) does not absorb noticeably. However, upon the enhancement of the concentration of **1** or, the use of cells with an optical path length of 5 cm, the tail of the UV absorption is observed in the visible spectral range up to 460 nm. The reaction kinetics was controlled by spectrophotometry by sampling with a syringe in a definite times and 100-fold dilution of the samples by ethanol.

The development of the reaction is remarkable. The induction time (from 7 to 20 min in dependence on the irradiation intensity) is observed. During this time, there are no changes in the absorption spectrum in the visible range, where λ^5 -phosphinoline **4** absorbs. Then the reaction develops spontaneously beginning locally either on a heterogeneous particle of ylide **1**, or on a cell wall, or on the solution surface that manifests itself by the appearance of a bright brown spot (Fig. 1). During 1–2 min, the reaction develops over the whole volume of the solution and is completed. The final solution is brown and transparent. Interestingly, when the reaction develops, the irradiation can be switched

off, and the reaction proceeds without irradiation. As one can see in Fig. 2, the absorption spectrum of the colored product registered in the visible spectral range corresponds to the absorption spectrum of λ^5 -phosphinoline **4**. One more peculiarity of the reaction is the observation that the sampling should be carried out carefully without mixing the solution. If the solution does be mixed, the reaction ceases and occurs with a new induction time. The addition of the stable reac-



Fig. 2. Changes in the absorption spectra of the mixture of **1** (0.024 mol L⁻¹) + **2** (0.1 mol L⁻¹) in CH₂Cl₂ during the photolysis (λ_{irr} 400 nm), photolysis time, min: (1) 0, (2) 7.0, (3) 8.0, (4) 9.0, and (5) the spectrum of λ^5 -phosphinoline (5.6 × 10⁻⁵ mol L⁻¹) in EtOH; inset, photolysis time, min: (1) 6.0 and (2) 7.0. For recording of the spectra, samples were diluted 100-fold with EtOH.

tion products, λ^5 -phosphinoline **4** and phosphonium salt **6** does not affect the reaction course. Methylene chloride CH₂Cl₂ is used as a solvent, because ylide **1** is poorly soluble in phenylacetylene.

The unusual development of the reaction allows for the proposal that the reaction occurs either by autocatalytic or chain mechanism, and the principal problem is the nature of products providing the autocatalysis or chain propagation and branching. Considering the reaction mechanism, one should take into account the following: (1) the reaction occurs under irradiation with the light with $350 < \lambda_{irr} < 450$ nm that means that **2** participates in the reaction in the ground state, and this is ylide **1** in the excited state that is the primary active species, and (2) the reaction proceeds very slowly in pure **2**, and the rate is significantly higher in methylene chloride solution. The proton elimination following from Scheme 1 is confirmed by the fact that pH of the aqueous extracts of the starting and final solutions shows a significant increase in the acidity of the mixture in the reaction course (pH 6.0 and 2.0, respectively).

Our experimental results obtained by the laser pulse photolysis of 1 in acetonitrile confirms the assumption that elimination of PhI and the formation of a transient species with the carbocationic structure (7) (Scheme 2, route *I*) is the primary photochemical reaction [5]. However, this photochemical reaction is only one of the possible routes. In the literature, both radical and radical cationic schemes of the transformations are considered for the photolysis of iodonium salts [8, 9]. Generalization of our and the literature data gives the following mechanism for the photodecomposition of ylide 1 (Scheme 2): iodobenzene and carbocation 7 are formed in route *I*, and radical 8 and radical cation of iodobenzene 9 are formed in route *2*.





The further transformation of cation 7 in the reaction with phenylacetylene 2 can occur via two routes. Route *1-1* is an electrophilic attack of the cation on the triple bond with a consequent step of electrophilic aromatic substitution to give λ^5 -phosphinoline 4 and proton elimination as we assumed in [7]. Route *1-2* is a reaction of cation 7 with the triple bond to give furan 5 similar to the formation of oxazoles in the photolysis of 1 in the nitrile solutions. As one can see in Scheme 2, route 2 affords radical 8 and iodobenzene radical cation 9. Radical 8 can abstract the hydrogen atom from the solvent, and the subsequent protonation gives enol 11 converting into a ketone form of salt 6 (Scheme 3). Interestingly, this process requires protons in the amount equivalent to the amount of the forming salt.



As was mentioned above, the appearance of protons in the medium is the result of the electrophilic substitution according to route 1-1 in Scheme 2. However, there is another route of the proton formation in the reaction of radical cation 9 with the solvent (Scheme 2, route 2). Since the ratio 8:9 = 1, because both intermediates are formed in the same reaction, and the proton is consumed in the salt 6 formation $(10 \rightarrow 11)$, the acidity of the reaction mixture as a whole is not increased in the route 2.

One point needs special consideration. Since proton is formed simultaneously with the formation of **4**, and the higher conversion degree of 1 into 4, the higher concentration of H⁺ in the solution, it is naturally to propose that, in this reaction, we deal with the acidic catalysis of the initiation step. In fact, the addition of acid (trifluoroacetic or *p*-toluenesulfonic acid) in the concentration higher than 0.15 mol/L initiates the formation of the products even in the absence of the irradiation. We propose that, at these acid concentrations, ylide 1 is protonated, and the protonation catalyzes its decomposition to give 4, PhI, and H⁺. As was mentioned above, initiation by the acid requires its high concentration.

On the basis of the study, the unusual development of the photochemical reaction between ylide 1 and phenylacetylene 2 can be represented as follows. Upon photoinitiation in the proximate vicinity to the heterogeneous particle, where the local concentration of the reagents is higher, the concentration of protons due to the photodecomposition of ylide in route 2 attains the critical value necessary for the acidic catalysis before than in the bulk solution. This induces the spontaneous development of the reaction catalyzed by the acid and its expansion over the bulk solution. Thus, the light plays the role of the initiator launching the spontaneous reaction.

The process under study is the example of the remarkable reaction, which can be considered as a chain reaction initiated by light or acid and catalyzed by one of the end products, proton. The possibility of the conversion of the photochemical reaction into the reaction catalyzed by acid will allow us further to study in detail the quantitative regularities of the reaction and to determine the kinetic parameters of the reaction and the critical concentrations of the reagents. This will give a key to control the direction of this complex photochemical–catalytic process.

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