# The Role of an Acid in the Decomposition of Mixed Benzoyl-Substituted Phosphonium–Iodonium Ylide

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Abstract—Mixed phosphonium—iodonium ylides allow the synthesis of not easily accessible and novel heterocyclic compounds. Photoinitiated reactions of phosphonium—iodonium ylides with acetylenes proceed with induction time and are catalyzed by acids, the acids formed in the reaction among them. The kinetic peculiarities of the reaction between the benzoyl-substituted phosphonium—iodonium ylide and trifluoroacetic acid were studied by UV-visible spectrophotometry. The kinetic parameters of the reaction were determined. The mechanism of the autocatalysis by acids has been proposed, which involves the formation of a protonated form of the ylide active in the decomposition into radical cations. The more active decomposition of the protonated ylide is confirmed by theoretical thermochemical calculations.

*Keywords:* phosphonium–iodonium ylides, acid catalysis, radical decomposition, theoretical thermochemical analysis

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## INTRODUCTION

Currently, mixed phosphonium—iodonium ylides, the compounds with several reactive centers, which general structure is given below, are studied in order to synthesize on their basis not easily accessible and novel heterocyclic compounds [1-3]:



where  $R^1 = Ph$  or five-membered aromatic heterocycle, and  $R^2 = CO(Ph)$ , CO(OMe), CO(OEt), CN,  $PO(OEt)_2$ ,  $S(O)_2(n-MeC_6H_4)$ .

The phenyliodonium group in the composition of mixed ylides determines their ability to decomposition under the action of light to afford active ionic and radical ionic transient species as was observed for diaryliodonium salts [4, 5]. Recently, two new photochemical reactions of mixed phosphonium–iodonium ylides with compounds with triple bond (C=N and C=C) were developed. As a result, substituted oxazoles (with nitriles) and furan derivatives and phosphorcontaining heterocycles (with acetylenes) are formed. The reaction with acetylenes is general for the phosphonium–iodonium ylides of different structure [6–11] and is given in Scheme 1 for the benzoyl-substituted ylide 1 (R<sup>1</sup> = Ph, R<sup>2</sup> = CO(Ph)) used in this investigation.



Scheme 1.

 $\lambda^5$ -Phosphinoline (3), furan derivative (4), and

phosphonium salt (5) (Scheme 1, counter ion  $BF_4^-$  is omitted in this and following schemes) are major reaction products. Photochemical reactions of acetylenes with phosphonium-iodonium ylide 1 proceeds only in dichloromethane at the ylide concentration exceeding 0.01 mol  $L^{-1}$  with an induction time [12, 13]. An acid is formed during the photolysis of the ylides and their mixtures with acetylenes in CH<sub>2</sub>Cl<sub>2</sub>. Therefore, it was proposed that the acid could play the role of a catalyst [13, 14]. It has been shown that the induction time of the reaction of ylide 1 with phenylacetylene decreases upon addition of strong organic acids (trifluoroacetic acid and toluenesulfonic acid) and the reaction becomes thermal, i.e., occurs without irradiation [13]. It is important that, to obtain the target product 3, the concentration of the added acid should not exceed the ylide concentration.

It is known that dichloromethane undergoes photoinduced radical reactions yielding HCl and phosgene [15–17]. Therefore, the reaction scheme of the ylide decomposition with implication of the solvent ( $CH_2Cl_2$ ) in radical reactions was suggested [14, 18]. It was assumed that generated hydrogen chloride could catalyze the photolysis and accelerate the reaction [14].

Therefore, here we studied the interaction of ylide **1** with trifluoroacetic acid (TFA) and considered the mechanism of autocatalysis with participation of acids with intermediate formation of the protonated ylide, i.e., a phosphonium–iodonium dication active in the decomposition on radicals and radical cations. The easier decomposition of the protonated form of ylide **1** yielding radical cations is confirmed within the framework of DFT calculations.

## **EXPERIMENTAL**

Ylide **1** was synthesized according to the procedure developed in [1, 7, 8]. Ylide was thoroughly washed by ether from the acid (HBF<sub>4</sub>) used in the synthesis. Dichloromethane (Etalon grade, Komponent Reactiv, Russia) without stabilizers and HCl and acetonitrile (High purity grade, Komponent Reactiv, Russia) were used without additional purification.

Absorption spectra were recorded on a Shimadzu UV3101 PC (Japan) spectrophotometer in quartz cells with an optical pathlength of 1.0 or 0.4 cm. Ylide **1** solutions  $(1 \times 10^{-4} \text{ mol } \text{L}^{-1})$  were prepared in CH<sub>2</sub>Cl<sub>2</sub> or acetonitrile. Calculated aliquots of the TFA stock solutions  $(1 : 10, [TFA] = 1.35 \text{ mol } \text{L}^{-1})$  in corresponding solvent were dropwise added by a micropipet into the ylide solution, with the acid addition decreasing the ylide concentration by less than 1%. In what follows in the text, the final TFA concentration in the reaction mixture is given. All measurements were carried out at room temperature in the air.

The kinetics of the reaction of ylide **1** with TFA in  $CH_2Cl_2$  were registered on a Shimadzu UV3101 PC spectrophotometer (Japan) in quartz cells with an optical pathlength of 1.0 cm in kinetic operation mode at the wavelength of 270 nm.

Mass-spectra were obtained on a 7T LTQ FT Ultra mass-spectrometer (Thermo Finnigan, Germany) with direct probe injection and a Finnigan Ion Max-Source universal ionization source in ESI regime (see for details [14]). Spectrophotometric investigations in the UV-visible range and mass-spectrometric measurements were carried out in the Shared Research Facilities of IBCP New Materials and Technologies.

Programs GAMESS US [19] with a PBE0 functional [20], 6-311++G(d,p) basic sets (involved in the GAMESS US program) for the H, C, O, and P atoms, and an aug-cc-pVDZ-pp basic set with an efficient core potential for the I atom [21] were used for the quantum chemical calculations. The geometry of ylide **1**, its protonated form, and all other particles formed in the decomposition of both ylide forms were optimized taking into account the solvation by dichlorometane using a model of polarization continuum [22]. All the studied systems were optimized without any restrictions except the fact that only doublet states were calculated for the particles with unpaired electron.

Vibrational analysis also performed with consideration for the solvation with dichloromethane confirmed that real minima on the potential energy surface corresponded to all optimized systems. The thermochemical analysis for all theoretically studied systems was carried out at 298.15 K (25°C). The Gibbs free energy changes ( $\Delta G_{298}$ ) at 25°C corresponding to the decomposition of ylide **1** and its protonated form were determined as a difference between the sum of the decomposition products free energies and the initial ylide free energy. To model the vertical excitations of **1** and its protonated form to their singlet states, a TD-DFT method [23] was used in combination with a PCM simulation of dichloromethane solvation.

## **RESULTS AND DISCUSSION**

## Interaction of Ylide 1 withTtrifluoroacetic Acid

Upon addition of an excess of TFA ( $5 \times 10^{-3} \text{ mol } \text{L}^{-1}$ ) into the ylide **1** solution ( $1 \times 10^{-4} \text{ mol } \text{L}^{-1}$ ) in CH<sub>2</sub>Cl<sub>2</sub> or acetonitrile, the product with an absorption spectrum close to the observed spectrum of transient species in the photolysis of ylide **1** of the same concentration in CH<sub>2</sub>Cl<sub>2</sub> is formed without irradiation (compare Fig. 1 with Fig. 1A in [14]). The rate of the reaction with TFA in CH<sub>2</sub>Cl<sub>2</sub> without irradiation is more than an order of magnitude higher than that in acetonitrile (Fig. 1, inset). It should be pointed out that in the ylide photolysis in acetonitrile in the presence of the acid, no derivative of oxazole, which is the major product of photoheterocyclization of **1** with acetonitrile in the absence of the acid [10], was found. The product



**Fig. 1.** Evolution of the absorption spectra of ylide **1** ([1] =  $1 \times 10^{-4}$  mol/L) in the presence of TFA ([TFA] =  $5 \times 10^{-3}$  mol/L) in acetonitrile; time, min: 0 (1), 5 (2), 10 (3), 20 (4), 30 (5), 45 (6), 63 (7), and 90 (8). Inset: kinetics of absorbance changes in acetonitrile (1, 2) and CH<sub>2</sub>Cl<sub>2</sub> (3, 4), registration wavelength, nm: 270 (1, 3) and 300 nm (2, 4).

formed in the decomposition of **1** in acidic solutions is stable without irradiation, but it is subjected to the photolysis during the irradiation of the reaction mixture by the light with the wavelength  $\lambda_{irr} < 365$  nm affording salt **5**. The spectral changes in the photolysis of **1** and in the reactions of **1** with TFA without irradiation are similar: the absorption increases in the wavelength range 260–290 nm and decreases at wavelengths >290 nm. However, the mass-spectrometric analysis of the photolysate of **1** in  $CH_2Cl_2$  upon photolysis completion [14] and of the solutions obtained in the reactions of **1** with TFA in  $CH_2Cl_2$  and acetonitrile without irradiation has shown that the products are different in these reactions. In both cases, the products of interaction of the ylide with acids, HCl in the photolysis and TFA upon acid addition, are major.

The major product of 1 with TFA, the ion with m/z = 493.12 Da  $(1 + TFA - PhI)^+$  in the mass-spectrum, is, probably, compound 8b, formed as a result of conversions shown in Scheme 2. In the mass-spectrometric analysis of the products of interaction of 1 with TFA in  $CH_2Cl_2$ , an unidentified molecular ion with m/z = 721.15 Da has been found. A molecular ion with m/z = 697.04 Da  $(1 + TFA)^+$  containing PhI in its composition has presented in trace amounts in both solvents. This ion belongs to the adduct of TFA to ylide 1 (7b). Compound 7b can also give the molecular ion with m/z = 493.12 Da in the ESI-MS analysis by PhI ejection. It is worth noting, that no chlorine-containing compounds 7a and 8a are formed in the reaction of ylide 1 with TFA in CH<sub>2</sub>Cl<sub>2</sub>, although these compounds were identified in the photolysis of diluted solutions of ylide 1 in  $CH_2Cl_2$  [14].

The following scheme for the interaction of acids (HA) with ylide 1 (Scheme 2) has been suggested on the basis of experimental results of this study on the dark interaction of 1 with TFA and the results obtained recently in the photolysis of 1 in  $CH_2Cl_2$  [14]:





Phosphonium–iodonium dication **6** is a product of reversible addition of proton to ylide **1**. The dication in the ionic pair  $[6 + A^-]$  enters into the reaction with an acid anion to give compound **7**. The presence of the traces of the molecular ion with m/z = 619.10 Da  $(1 + HCl)^+$  in the photolysis of **1** in CH<sub>2</sub>Cl<sub>2</sub> [14] (compound **7a**) and with m/z = 697.04 Da  $(1 + TFA)^+$  (compound **7b**) in the reaction of **1** with TFA confirms this. It follows from our studies that ions formed as a result of detachment of PhI are identified mainly in the ESI-MS analysis of the phenyliodonium compounds. Compounds **8** are the products of further conversion of **7**. The forma-

tion of compounds similar to 7 and 8 was suggested in [24] in the study of  $S_N 2$  substitution in alkylvinyl(phenyl)iodonium salts. Here we have shown that the product of addition of the anion (A<sup>-</sup>) to the iodonium group 7 is unstable, ejects PhI, and fast coverts into 8. Based on these results, we propose that the reaction of dication 6 with the acid anion to give 7 is the limiting step of conversion of dication 6 into final product 8.

According to spectrophotometric investigation of the kinetics of the ylide 1 reaction with TFA excess (registration at 270 nm) (Fig. 2a), the absorption changes are approximated adequately by exponential



**Fig. 2.** (a) Kinetics of absorbance changes  $\Delta A = A_t - A_0$  at  $\lambda_{reg} = 270$  nm in the mixture of ylide **1** ([1] = 1 × 10<sup>-4</sup> mol/L) and TFA in CH<sub>2</sub>Cl<sub>2</sub> as a function of the TFA concentration (mol/L): 0.00045 (1), 0.00135 (2), 0.0027 (3), 0.0045 (4), and 0.0135 (5); (b) dependence of the rate constant of absorbance changes ( $k_{obs}$ ) on the TFA concentration.

functions, with the rate constant for the product formation  $(k_{obs})$  being a linear function of the TFA concentration (Fig. 2b), and the bimolecular efficient rate constant for the formation of the products of the ylide 1 reaction with TFA ( $k_{eff}$ ) being 1.5 ± 0.1 L mole<sup>-1</sup> s<sup>-1</sup>. Within the framework of the proposed mechanism of the interaction of mixed phosphonium-iodonium ylide 1 with acids (Scheme 2), the linear dependence of the rate constant vs. the acid concentration implies that K[HA]  $\ll$  1, and the experimental  $k_{\text{eff}} = k_1 K$ . The highest concentration of the acid in our experiments was  $[TFA] = 0.014 \text{ mol } L^{-1}$ , i.e.,  $K \ll 70 \text{ L mol}^{-1}$ . The low value of the equilibrium constant means that the equilibrium concentrations of dication 6 in the mixture are low. In fact, if  $K = 5 \text{ L mol}^{-1}$ , the equilibrium concentration of **6** is  $\sim 5 \times 10^{-6}$  mol L<sup>-1</sup> at [**1**] = 1 × 10<sup>-4</sup> mol L<sup>-1</sup> and  $[TFA] = 1 \times 10^{-2} \text{ mol } L^{-1}$ , i.e., only 5% of the initial ylide 1 concentration. This is probably caused by the fact that dication 6 with double positive charge is formed instead of cation 1. It is likely that the stability of this dication should not be very high. Probably, this is the reason why 6 either converts back into 1, or decomposes on 10 and PhI++ (see further reaction (II)), or stabilizes by conversion into 7 with a lower (+1) positive charge.

The complex character of the ylide **1** reaction with an acid and its subsequent transformations is confirmed by the dependence of the absorption spectra of the ylide mixture with TFA on the TFA concentration (Fig. 3). If the acid concentration in the mixture at zero time does not exceed the ylide concentration, the absorption spectrum practically does not vary during 15 min confirming the low concentration of dication 6. The further increase in the acid concentration increases the absorbance in the range 260-286 nm, with the solution absorbance at  $\lambda > 286$  nm being almost the same for several minutes up to the tenfold increase in the acid concentration. (Fig. 3a). In 15 min, the absorption spectrum varies in dependence on the TFA concentration: when the TFA concentration increases, the absorbance at  $\lambda > 286$  nm decreases similar to that observed in time after addition of the large TFA excess (compare Fig. 3b and Fig. 1). When the observation time increases, the isosbestic points shift (Figs. 3a and 3b) also indicating the complex character of the reaction between ylide 1 and the acid.

## Theoretic Thermochemical Analysis of Decomposition of Ylide **1** and Its Protonated Form **6**

Recently, it has been assumed that phosphonium– iodonium dication 6, the protonated ylide 1, is more active in the decomposition onto radical intermediates than the parent ylide [14] (here and further on we

neglect the influence of the counterion  $BF_4^-$  on the properties of **1** and dication **6**), and its formation *in situ* in the reaction of **1** with HCl (generated from the solvent, dichloromethane) or with the added acid accel-



**Fig. 3.** Absorption spectra of ylide 1 ([1] = $1.0 \times 10^{-4}$  mol/L) in 1 (a) and 15 (b) min after addition of TFA in concentrations (10<sup>4</sup>, mol/L): 0 (1), 0.6 (2), 2.0 (3), 5.0 (4), 10 (5), and 20 (6). Inset: dependence of absorbance on concentration of TFA at wavelength (nm): 270 (1, 1'), 300 (2, 2') in 1 (1, 2) and 15 min (1', 2'); CH<sub>2</sub>Cl<sub>2</sub> solvent.

erates the synthesis of final products due to an increase in the initiation rate. To confirm the assumption that dication **6** decomposes on radical and radical cation species more readily than ylide **1**, the theoretic thermochemical analysis of reactions (I) and (II) was carried out taking into account the solvation with dichloromethane with the use of the model of polarized continuum.

$$\begin{array}{ccc} Ph_{3}P^{+} & O^{-} & Ph_{3}P^{+} & O^{-} \\ PhI & Ph & Ph & Ph \\ 1 & Ph & Ph & Ph \end{array}$$
(I)
$$\begin{array}{ccc} 1 & 9 \end{array}$$

$$(Ph)_{3}P^{+}_{C} = C \xrightarrow{OH}_{PhI} Ph_{3}P^{+}_{C} = C \xrightarrow{OH}_{Ph} + (PhI)^{+} (II)$$

$$6 \qquad 10$$

The PBE0 calculations show that the change in the Gibbs free energy ( $\Delta G^{298}$ ) in reactions (I) and (II) at 298 K (25°C) is according to the thermochemical analysis 42.6 kcal mol<sup>-1</sup> (178 kJ) and 21.2 kcal mol<sup>-1</sup> (89 kJ), respectively. The enthalpy for reactions (I) and (II) at 25°C increases by 58.1 kcal mol<sup>-1</sup> (244 kJ) and 38.5 kcal mol<sup>-1</sup> (161 kJ), respectively. Thus, the calculations confirm qualitatively the distinctly lower stability of dication **6** (reaction (II)) to the decomposition in comparison to the decomposition of parent ylide **1** (reaction (I)). The elongation of the bond between the iodine atom and the carbon atom (C2–I) linked with the c PPh<sub>3</sub> group from 2.063 Å in **1** to

2.094 Å in **6** and shortening of the bond length between the iodine atom and the carbon atom of the phenyl group from 2.137 Å in **1** to 2.128 Å in **6** are supplementary evidences of higher tendency of **6** to decomposition (i.e., to the ejection of the radical cation (PhI)<sup>•+</sup>). The Mulliken charges on the iodine atom in **6** and **1** are 0.594 and 0.606, respectively. In (PhI)<sup>•+</sup> the C–I bond length is 2.038 Å, and the charge on the iodine atom is 0.578. Thus, the calculations show that **6** is more prepared to the (PhI)<sup>•+</sup> ejection than **1**. Possibly, this is the reason for the easy decomposition of the protonated form of **1** onto two radical cations.

#### The Mechanism of Acid Catalysis in the Photolysis of Ylide 1

Since the theoretical analysis of the decomposition of ylide 1 and dication 6 formed from this was carried out for thermal reaction, the question arises about application of these results to the photolytic decomposition of ylide 1. Thoroughly purified crystalline ylide 1 is stable and can be stored almost without changes for several months. However, being dissolved in  $CH_2Cl_2$ , ylide 1 converts to the products, with salt 5 being the major, in the dark during one to several days. The dark conversion is accelerated by the traces of an acid that corresponds to the calculated data for the dication 6 decomposition. Under irradiation, the ylide 1 in  $CH_2Cl_2$ solution (0.05 mol  $L^{-1}$ ) is consumed completely during 1 h, with salt 5 being the major product similarly to the dark process. Thus, the decomposition of

 Table 1. TD-DFT modeling of optical vertical excitation of ylide 1 and its protonated form 6 in dichloromethane to corresponding singlet states\*

Singlet state	1			6		
	$\lambda_{ex}$ , nm	$E_{\rm ex}$ , eV	f	$\lambda_{ex}$ , nm	$E_{\rm ex}$ , eV	f
1	355.25	3.4900	0.0038	363.71	3.4088	0.0067
2	316.45	3.9180	0.0159	354.65	3.4960	0.0094
3	293.94	4.2180	0.0861	338.58	3.6619	0.0166
4	292.09	4.2448	0.0029	330.69	3.7493	0.0944
5	276.50	4.4841	0.0136	290.32	4.2706	0.0012

\*  $\lambda_{ex}$  is the excitation wavelength,  $E_{ex}$  is the excitation energy, f is the occilator strength.

ylide **1** under irradiation and in the dark occurs with formation of radical intermediates and the same final products, with the rate of their formation being significantly higher in the photolysis. Both neutral radicals and radical cations are meant as radical intermediates.

The decomposition of 1 in the presence of the acid traces is accelerated also in the photolysis. The irradiation of 1 and dication 6 should excite them to singlet states. TD DFT modeling of the optical vertical excitation of ylide 1 and dication 6 to the corresponding singlet states  $1^*$  and  $6^*$  in dichloromethane shows that the probability of vertical excitation of 1 to the first singlet state is almost twice lower than that for 6 at relatively close excitation energies for 6 and 1 (Table 1). Therefore, the generation of the first excited singlet state and its further decomposition are more probable for 6 upon irradiation of the mixture of 1 and 6.

According to the values of 
$$E_{ex}$$
 and  $f$  (Table 1), the excitation of **6** into the singlet states 2–4 is more probable than the similar excitation of **1**.

We assume that, similarly to the dark reactions (I) and (II), the Gibbs energies for the conversion of the singlet states of 6\* into (PhI)<sup>++</sup> and radical cation 10 will be lower than those for the conversion of the singlet states of  $1^*$  into  $(PhI)^{\bullet+}$  and 9. This implies that the photolytic decomposition of **1** in dichloromethane also should be accelerated by acids that is confirmed by experimental data. It is reasonable to expect that  $\Delta G^{298}$  for the excited singlet states of **6**\* and **1**\* should be significantly lower than  $\Delta G^{298}$  for decomposition of 6 and 1 in the ground state, i.e., the decomposition of 1 in the photolysis should be noticeably faster. To confirm these assumptions, it is necessary to carry out additional quantum chemical investigation of 6\* and 1\* and the thermochemical parameters of their decomposition. This is a separate problem.

The further transformations of radical intermediates (PhI) $^{\bullet+}$ , **9**, and **10** proceed according to reactions (III)–(VI):

$$(PhI)^{+} + CH_2Cl_2 \longrightarrow PhI + CHCl_2 + H^{+}$$
(III)

$$\begin{array}{ccc} Ph_{3}P^{+} & O^{-} & Ph_{3}P^{+} & O\\ C = C & +H^{+} & \longrightarrow HC = C & \\ Ph & & 11 \end{array}$$
(IV)

$$\stackrel{Ph_{3}P_{\cdot}^{+}}{\stackrel{O}{C}=C} \stackrel{OH}{\longleftarrow} \stackrel{Ph_{3}P_{\cdot}^{+}}{\stackrel{O}{\longleftarrow}} \stackrel{O^{-}}{\underset{Ph}{\longrightarrow}} H^{+} \qquad (V)$$
10 Ph 9 Ph

$$\begin{array}{ccccccccccccc} Ph_{3}P^{+}, & OH & Ph_{3}P^{+}, & O^{-} & Ph_{3}P^{+}, & O^{-} & (Ph)_{3}P^{+}, & OH \\ C = C & + & + & C = C & & \\ Ph & PhI & Ph & PhI & Ph & \\ 10 & 1 & 9 & 6 & & \end{array}$$
(VI)

The conversion of transient radicals **9** and **10** into the radical cation **11** is the result of reactions (III)– (VI). The PBE0 calculations with regard to the solvation by dichloromethane show that the free energy of the radical cation **11** at 25°C is by 22.4 kcal mol<sup>-1</sup> (94 kJ) lower than that for **10**. In other words, **11** is by 22.4 kcal mol<sup>-1</sup> thermodynamic more favorable than **10**.

In fact, radical cation **11** is relatively stable, and its structure was suggested based on the quantum chemical calculation of the possible structure for the radical cation registered by EPR in the photolysis of ylide **1** [18]. In reaction (VII) of this radical with the solvent, phosphonium salt **5**, the major product of the ylide transformations [18], and the radical  $\cdot$ CHCl<sub>2</sub> are formed:

$$\begin{array}{c} \overset{Ph_{3}P^{+}}{HC} \stackrel{O}{-C_{Ph}} + CH_{2}Cl_{2} \xrightarrow{\dot{-CHCl_{2}}} Ph_{3}\overset{Ph}{PCH_{2}C} \overset{Ph}{\leq} \\ \overset{Ph}{11} \qquad 5 \end{array}$$
(VII)

The autocatalysis in the ylide **1** photolysis by hydrogen chloride can be performed due to photolytic and dark reactions of the solvent radical  $`CHCl_2$  (formed in reactions (III) and (VII)) in reactions (VIII)–(X), in which hydrogen chloride is generated [15–17]:

$$\dot{C}HCl_2 \xrightarrow{hv} \dot{C}Cl + HCl$$
 (VIII)

$$\dot{C}HCl_2 \xrightarrow{O_2} CHCl_2\dot{O}_2 \xrightarrow{H_2O} COCl_2 + \dot{O}H$$
 (IX)

$$\operatorname{COCl}_2 + \operatorname{H}_2 \operatorname{O} \longrightarrow \operatorname{CO}_2 + 2\operatorname{HCl}.$$
 (X)

The excess of the added acid removes the ylide from the reaction, because it shifts the equilibrium (Scheme 2) to further conversion of reactive dication **6** to compounds **7** and **8**, which are not the initiators of the radical reactions. The conversion of **6** to **7** occurs in the bimolecular reaction with the acid anion. The increase in the acid concentration increases the concentration of the anion and consequently accelerates the reaction. This accounts for the experimental observation that no target heterocyles **3** and **4** are formed in the presence of acetylenes at the excess of the acid [13]. The regularity of the reaction between mixed phosphonium–iodonium ylides and acetylenes will be considered in detail in following publications.

In theory, when ideally pure ylide 1 is used, the decomposition of the ylide itself should be a reaction trigger, which launches reaction sequence (I)-(X). However, we cannot exclude that the initiation of the reaction both under and without irradiation is mainly caused by the radical decomposition of dication 6, rather than of the parent ylide 1. This is indicated by the dependence of the photolysis initial rate on the purification degree of different phosphonium-iodonium ylides from the traces of HBF<sub>4</sub>, which is used in their synthesis. The synthesized ylide 1 may contain the traces of protonated ylide, dication  $\mathbf{6}$ , even after very thoroughly washing from HBF<sub>4</sub> by ether, and the primary initiation occurs on the dication due to the formation of radical cations (PhI)<sup>++</sup> and 10. These radical cations generate new protons in reactions (III) and (V), respectively, which assist to the appearance of dication  $\mathbf{6}$ , and further on the reaction develops in autocatalytic regime due to the formation of hydrogen chloride from the solvent in reactions (III), (VIII), and (X). The addition of a base  $(Et)_3N$  into the solution of ylide 1 inhibits its photolytic and dark reactions confirming the role of acids in the reaction initiation.

### CONCLUSIONS

Experimental spectrophotometric investigation of the interaction of benzoyl-substituted mixed phosphonium-iodonium ylide 1 with trifluoroacetic acid and the theoretical thermochemical calculations have shown that the phosphonium-iodonium dication is substantially more active in the decomposition on radical cations than the parent ylide. The autocatalytic character of the photolysis of the phosphoniumiodonium ylide is caused by the hydrogen chloride generation in the conjugated radical reaction of dichlorometane. More reactive phosphonium-iodonium dication 6 is formed in the reaction of hydrogen chloride with the parent ylide. This increases the rate of the formation of radical cations active in further ylide reaction and simultaneously inducing radical reactions of the solvent causing the appearance of HCl. The regularities revealed for the photolytic decomposition of 1 are possibly applicable to the decomposition of other mixed phosphonium-iodonium ylides.

It is shown that, at the excess of the acid, the protonated form of ylide 1 formed in its reaction with the acid converts to compound 8, which does not participate in the subsequent ylide reactons. The mechanism for the interaction of acids with mixed ylides is suggested, the products of the interaction are characterized, and kinetic parameters for the reaction of ylide 1 conversion to compound 8 are estimated.

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