RESEARCH ARTICLE

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Dichloromethane as solvent and reagent: a case study of photoinduced reactions in mixed phosphonium-iodonium ylide

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Abstract

Several years ago the photoinduced reaction of mixed phosphonium-iodonium ylides (1) with acetylenes (2) to give λ^5 -phosphinolines (3) and substituted furans (4) was described. This reaction is one-pot, metal-free synthesis of heterocycles 3 and 4 with the yields of 40% to 80%. The reaction proceeds only in dichloromethane (DCM) at the high vlide concentrations (>0.01 mol/L). The product analysis by ³¹P NMR, electrospray ionization mass spectrometry, UVvis spectrophotometry, and the dynamic light scattering study of the self-aggregation of the ylide in DCM showed a dual role of the solvent in the photoinduced reactions of mixed phosphonium-iodonium ylide: (i) at the low ylide concentrations (<0.01 mol/L), the conjugated photoinitiation of the chain reaction in DCM results in the formation of chlorine-containing products and (ii) at the high ylide concentrations (>0.01 mol/L), the photolysis mechanism is determined by self-organization of the ylide molecules to give large stable aggregates in DCM, in which the target heterocycles are synthesized. Two important issues follow from the study. First, the annulation reaction between mixed phosphonium-iodonium ylide and acetylenes occurs only when the reactive intermediates are in close proximity to one other, and, second, DCM is not inert reagent in reactions occurring with participation of radicals and in one form or another can participate in photoinduced radical reactions of various solutes.

KEYWORDS

annulation with acetylenes, dichloromethane, phosphonium-iodonium ylides, radical reactions, self-assembly

1 | INTRODUCTION

Iodonium compounds attract considerable attention due to their wide application in organic synthesis^[1-4] and in

photoinduced initiation of cationic polymerization.^[5–7] A great variety of reactions occurring with participation of iodonium compounds involve radicals. For a long time, radical reactions, especially chain reactions, were

This article is dedicated with respect and affection to the memory of the late Prof. Nikolay S. Zefirov.

considered as unsuitable for synthetic purposes because of their low selectivity. Currently, the interest to radical mechanisms in organic synthesis increases substantially.^[8-10] It has been found that some reactions, which were not considered earlier as reactions with participation of radicals, are in fact radical reactions in disguise. Some of these reactions were carried out in dichloromethane (DCM) as a solvent.^[1b,c,3] Dichloromethane is widely used in organic synthesis for reactions proceeding at the temperatures below 40°C. The low boiling point of the solvent allows for easy separation of reaction products. Despite the relatively low polarity, a great variety of polar and nonpolar compounds are soluble in DCM in concentrations required for the synthesis. On the other hand, it has been well documented that DCM is not stable and is subjected to radical chain reactions under the action of UV light in the presence or in the absence of photosensitizers, oxygen, or water.^[11–14] The radical chain reactions of DCM and other chlorinated hydrocarbons have been described not only for atmospheric transformations (see Spence et al^[14] and references therein) but also for the bulk and water solutions.^[12,13] Independent of the medium, the major products of these reactions are various chlorinated hydrocarbons formed in propagation and termination steps, HCl, and phosgene in the presence of oxygen. This raises the question about feasible participation of the solvent in radical reactions of solutes.

Several years ago the photoinduced reaction of various mixed phosphonium-iodonium vlides (1) with different acetylenes (2) to give λ^5 -phosphinolines (3) and substituted furans (4) was described (Scheme 1; in all schemes, counterion BF_4^- is omitted).^[15,16] This reaction is one-pot, metal-free synthesis of heterocycles 3 and 4 with the yields of 40% to 80%. The ratio of the yields of 3 and 4 depends on the ionization potential of acetylenic compounds: the lower ionization potential, the higher vield of the furan derivative 4.^[15,16] In the case of phenylacetylene, **4** is formed in a trace amount (<5%), and the yield of λ^5 -phosphinoline **3** attains 60%. Recently, phosphorus π -conjugated molecules have attracted growing attention due to their potential application as functional materials,^[17] and from this point of view, the reaction under study is of interest, because it provides simple synthesis of P-containing heterocycles.

The reaction is characterized by remarkable peculiarities.^[18] The formation of heterocycles **3** and **4** occurs only in DCM at $[1] \ge 0.01$ mol/L. The ylide 1 is not soluble at such concentrations in EtOH, hexane, and dichloroethane, and the photochemical cyclization with acetylenes does not occur in these solvents. Acetonitrile is not suitable solvent for the reaction between ylides and acetylenes, because the ylides undergo photoinduced reaction with ACN to give 2,3,5-substituted oxazoles.^[19,20]

The reaction with acetylenes occurs with an induction time (4-30 min) depending on the light intensity and the purity of the ylide and DCM and then develops during several minutes.^[18] (Figure S1) It has been shown that addition of an acid decreases the induction time.^[21]

To resolve the problems concerning the mechanism of photoinduced reactions in mixed phosphonium-iodonium ylides, the kinetics of the photolysis of ylide **1** (R = Ph) alone and in its mixture with phenylacetylene (**2**) was studied by UV-Vis spectrophotometry, ³¹P NMR, and electrospray ionization mass spectrometry (ESI-MS) in a wide range of ylide concentrations. Here the results of the study demonstrating the role of DCM in the photoinduced reactions of ylide **1** are presented.

2 | EXPERIMENTAL

2.1 | General procedure

Ylide 1 was synthesized according to the procedure described elsewhere and was thoroughly washed from HBF₄.^[22] Dichloromethane (DCM) (Etalon grade, Komponent Reactive, Russia) without stabilizer was used as received. Phenylacetylene 2 was distilled before use. A weighted portion of 1 (0.01 mmol, 6.7 mg) was dissolved in DCM (1 mL) by sonication in an ultrasonic bath. To obtain the solutions with low concentration ($\sim 10^{-4}$ mol/ L), the solutions were diluted 100-fold with DCM. To prepare the ylide solution with the concentration of 0.05 mol/ L, a weighted portion of 1 (0.1 mmol, 67.0 mg) was dissolved in DCM (2 mL) by sonication in an ultrasonic bath. It should be pointed out that since this is the mechanistic study, all yields were obtained from the ³¹P NMR spectra for the final and intermediate reaction mixtures without isolation of the products. The yields of the target products after isolation have been given elsewhere.^[15,16] Hereafter, we use the terms low concentrations for the ylide concentrations $\sim 10^{-4}$ mol/L and high concentrations for the concentrations >0.01 mol/L.



SCHEME 1 Principal scheme of the photoinduced reaction of mixed phosphonium-iodonium ylides with acetylenes

2.2 | UV-vis spectrophotometry

UV-vis spectra were measured on a Shimadzu UV3101 PC spectrophotometer in a quartz cell with an optical pathlength of 1.0, 0.4, or 0.2 cm. The kinetics at the low concentration was recorded after successive irradiation for fixed times. In the case of large concentrations, the solutions after irradiation for fixed times were diluted in 50 to 100 times with DCM.

2.3 | ESI-MS measurements

Mass spectrometry spectra were obtained by 7T LTQ FT Ultra mass spectrometer (Thermo Finnigan, Germany) using direct sample injection and ESI. Electrospray ionization parameters were the following: high voltage +3.0 kV (positive mode), desolvation capillary temperature 200°C, and solvent flow 4.0 μ L/min. The samples were protected from light all the time by covering vials, transparent ESI source parts by aluminum foil. All samples were diluted to ~10⁻⁶ mol/L.

2.4 | ³¹P NMR spectroscopy

¹H-decoupled ³¹P NMR spectra were registered on an AVANCE 500 spectrometer (Bruker, Germany) in reaction mixtures in DCM. The spectra in the kinetic measurements of the photolysis at the high concentration were monitored in 256 scans (~2.5 min), and the final spectra were measured in 512 scans (~5 min). The spectrum of the final products of the photolysis at the low concentration was measured after irradiation of the solution (100 mL) in DCM with a LED 365 ([365 ± 10] nm) for 40 minutes, evaporation of DCM on a rotor evaporator and dissolution of the residue in CDCl₃.

2.5 | Dynamic light scattering measurements

Sizes of ylide particles in DCM were determined with a Zetasizer Nano ZS dynamic light scattering (DLS) spectrometer (Malvern, United Kingdom) at the wavelength of 633 nm at 25°C. A stock solution (0.05 mol/L) was prepared by sonication of a weighted portion in DCM. Solutions with concentrations from 0.01 to 10^{-5} mol/L were prepared by successive dilutions of the stock solution followed by sonication. Before measurements, the solutions were equilibrated for 15 minutes. The experimental data were averaged over 5 consecutive cycles of the measurements.

2.6 | General procedures of the photolysis of ylide 1 and its mixtures with phenylacetylene 2

The photolysis of $\mathbf{1}$ at the low concentrations was carried out in a quartz cell with a pathlength of 1.0 or 0.4 cm with a light of a DRSh-2000 high-pressure mercury lamp isolating the lines 313 or 365 nm by a set of glass filters or with the use of a LED 365 nm. Absorption spectra were registered in fixed time intervals on a Shimadzu UV3101 PC spectrophotometer.

The photolysis of **1** at the high concentrations was carried out with LEDs 365, 400, or 450 nm either in an NMR tube (0.5 mL) with registration of the 31 P NMR spectra in a fixed time of irradiation or in a glass tube (2 mL) with taking out the aliquots (0.02 mL) in fixed time intervals, dissolving this in 2.0 or 1.0 mL of DCM and measuring the UV-vis absorption spectra in a quartz cell with a pathlength of 0.4 cm.

The kinetics of the photoinduced reaction between ylide **1** and phenylacetylene **2** was measured after irradiation of the mixture **1** (0.05 mol/L) + **2** (0.15 mol/L) for 20 seconds in an NMR tube by LED 365 nm, then loading the tube in a spectrometer resonator and measuring the ³¹P NMR spectra in 256 scans in succession.

3 | RESULTS

3.1 | Photolysis of ylide 1 at different concentrations

The product composition in the photolysis of **1** depends on the ylide concentration. At the low concentrations, the photolysis of **1** occurs under UV irradiation (λ_{irr}) 365 nm) and results in the formation of a reaction product with $\lambda_{max} = 271$ nm (Figure 1A,D). The product is relatively stable under irradiation with $\lambda_{irr} = 365$ nm but is subjected to further transformations under irradiation with $\lambda_{irr} = 313$ nm or under long-term storage with formation of a product with $\lambda_{max} \sim 261$ nm (Figure 1B, D). The reaction shows clearly observed 2-step character and can be interrupted at the first step. At the high concentrations, the photolysis occurs at $\lambda_{irr} \leq 450$ nm to afford the major product with $\lambda_{max} = 261$ nm coinciding with that formed in the second step at the low concentrations (Figure 1C,D) and corresponding to the absorption maximum of salt 5 (Scheme 1) (Figure S5).

The ESI-MS analysis of the final product mixtures shows the presence of Cl-containing compounds by characteristic isotopic pattern (ESI; Figure S2A,B). Two molecular ions containing chlorine atoms are observed at the low concentrations: M^+/z 415.1013 (100%) and 477.0561 (64%) (Figure S2A). The former corresponds to



FIGURE 1 Evolution of the absorption spectra of **1** (A) under irradiation with $\lambda_{irr} \le 365$ nm and (B) under further irradiation with $\lambda_{irr} = 313$ nm, [**1**] = 1×10^{-4} mol/L, DCM; (C) under irradiation with $\lambda_{irr} \le 450$ nm, [**1**] = 0.05 mol/L, DCM; and (D) differential spectra ($\Delta A = A_{final} - A_{ylide}$) of final product mixture for different initial concentrations of **1**: 10^{-4} mol/L first step (dark blue), 10^{-4} mol/L second step (blue), and 0.05 mol/L (red)

empirical formula $C_{26}H_{21}ClOP^+$ an (HRMS_{theor} = 415.1019) and the latter to $C_{27}H_{20}O_2Cl_2P^+$ (HRMS_{theor} = 477.0572). Other molecular ions detected in the mixture are M^+/z 381.1398 (35%, phosphonium salt 5, HRMS_{theor} = 381.1408), M⁺/z 353.1448 (27%, empirical formula $C_{25}H_{22}P^+$, HRMS_{theor} = 353.1454), and M⁺/z 279.0929 (18%, protonated triphenylphosphine oxide $Ph_3P = O + H^+$, HRMS_{theor} = 279.0939) The formation of the latter has been always observed in the photolysis of 1 in DCM and ACN and has been accounted for by photochemical reactions of salt 5.^[20,23] The molecular ion M^+/z 353.1448 corresponds to $Ph_3P^+CH_2Ph$. The product composition after the storage of the solution for a day changes M^+/z 279.09 (15%), 353.14 (5%), 381.14 (100%), 415.10 (19%), and 477.06 (6%) confirming specrophotometric data on the conversion of the products of the first step to salt 5.

At the high concentrations of **1**, the overall picture of the photolysis changes. First, the boundary wavelength of the irradiating light shifts to the red up to 450 nm. The consumption of **1** and the formation of the reaction products measured by ³¹P NMR occur with slight acceleration (Figure 2). Comparison of the ESI-MS and ³¹P NMR spectra (Figure 3 and full-scale spectrum in Figure S3) of the final product mixtures shows that salt 5 is a major product (~40% to 50%) at the high concentrations. The formation of Cl-containing product with M^+/z 415.1013 is also observed in this case, but in much lower relative concentration than at the low ylide concentrations. When the reaction course is monitored by ³¹P NMR, 2 more products with $\delta = 44.5$ (~10%) and 50.9 (~16%) ppm and several minor products in the range 23 to 26 ppm are observed. The relatively large concentration of the product at 28 ppm for the low concentration allows for the assumption that this may be one of the Cl-containing compounds (compare ³¹P NMR spectra A and B in Figure 3). Two signals at 25 ppm may also be assigned



FIGURE 2 Consumption of ylide **1** in the photolysis alone and in the mixture **1** + **2** in DCM

to the Cl-containing products. Unfortunately, we failed to isolate and identify minor products from the reaction mixture. It should be pointed out that the signals at $\delta = 44.5$ and 50.9 ppm as well as the signals of minor products at 24 and 26 to 27 ppm appear with a delay relative to salt **5**, indicating that these are the products of further conversions.

3.2 | Photolysis of ylide 1 with phenylacetylene

As mentioned above, the reaction of ylides with acetylenes does not occur at the ylide concentrations lower than 0.01 mol/L. At the higher concentrations, the photoinduced reaction between ylide **1** and phenylacetylene **2** proceeds under continuous irradiation with an induction time, and no products containing ³¹P with an accuracy of the ³¹P NMR spectrometry are observed during the induction time; ie, in the presence of **2**, the photoinduced



FIGURE 3 Partial ³¹P NMR spectra of the final photolysis products of ylide **1**: (A) 10^{-4} mol/L after evaporation and dissolution of the residue in CDCl₃ and (B) 0.05 mol/L; (C) after photolysis of the mixture **1** (0.05 mol/L) + **2** (0.15 mol/L); (B) and (C) final reaction mixtures in DCM

reaction of **1** is inhibited (Figure 2). When the induction time is over, the consumption of **1** occurs much faster than in the absence of **2** with the products composition changing crucially from that for the ylide photolysis: λ^5 phosphinoline **3** (δ = 2.51 ppm, Figure 3C, and M⁺/*z* 481.1699 [**3** + H⁺]; Figure S2C) is a major product (~50%), the yield of salt **5** (~7%) and the products with δ = 44.5 and 51 ppm (<2% each) decreases dramatically (Figure 3 and full-scale spectrum Figure S3). No detectable amounts of Cl-containing products were found in the final reaction mixture by ESI-MS (Figure S2C) and ³¹P NMR (Figure 3C).

3.3 | Self-assembly of ylide molecules in the DCM solution

Pure ylide **1** is a white crystalline substance. Being solved in DCM in the concentration up to 0.005 mol/L, a colorless transparent solution is formed. When the ylide concentration is increased, the solution becomes light yellow, and at the concentrations higher than 0.01 mol/ L, slight opalescence is observed. The ylide precipitation is not observed up to the concentration of 0.2 mol/L. This result allows for the assumption that self-assembly of the ylide molecules occurs, when the ylide concentration in

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DCM increases, and the ylide aggregates form stable microheterogeneous system. Interestingly, such behavior is observed only in the ylide solutions in DCM. When the ylide is dissolved in other solvents (EtOH, AcN, DMSO, and $C_2H_4Cl_2$), the formation of microheterogeneous system is not observed, and after exceeding some limiting concentration, which is different for various solvents, ylide precipitates as white crystals.

The variations in the ylide absorption spectra in a wide concentration range (5×10^{-6} -0.1 mol/L) show that up to the concentration of 10^{-4} mol/L, the absorbance at different wavelengths almost linearly depends on the ylide concentration (Figure 4). The observed deviation from the linearity on the further increase in the concentration indicates the formation of aggregates. The next inflection point in the dependence of the absorbance on the ylide concentration is observed near 0.01 M, and the light scattering manifests itself at the concentrations >0.01 M by the nonzero absorbance at $\lambda > 470$ nm (Figure 4).

The investigation of the ylide solutions in DCM by the DLS technique shows that self-assembly of the vlide molecules occurs in time even for very low concentrations. The equilibrium is established in 15 minutes after sonication of the solutions. The size of the aggregates depends on the ylide concentration, and even at the concentration of 10^{-5} mol/L, the aggregates (up to 175 nm) are observed. In the concentration range from 0.001 to 0.01 mol/L, the particle size increases crucially (Figure 5). At the concentrations higher 0.01 mol/L, the mean particle size does not depend on the concentration and is near 900 nm with relatively narrow particle distribution by size (Figure S4). More detailed



FIGURE 4 Absorption spectra of ylide **1** at various concentrations; inset, dependence of the absorbance at different wavelengths on the ylide concentration



FIGURE 5 Dependence of the particle size on the ylide concentration

examination of the microstructure of the ylide solutions at the high concentrations is in progress.

4 | DISCUSSION

Iodonium salts are able to decompose under the action of light to give ions, radicals, and radical cations.^[1b,3,5-7] Ylide **1** being a iodonium compound decomposes under the action of light (Scheme 2). Formation of relatively stable radicals in the photolysis of **1** and in the mixtures with acetylenes in DCM was shown by electron paramagnetic resonance, and registered radical **8** is formed in the interaction of primary radical **6** with H⁺.^[24] According to Scheme 2, salt **5** is the major product of the ylide **1** photolysis in DCM and this is the case at [**1**] > 0.01 mol/L.

As follows from Scheme 2, the solvent is involved in the reaction, and 2 hydrogen atoms in **5** originate from the solvent. In fact, the formation of salt **5** with 2 deuterium atoms $Ph_3P^+CD_2COPh$ was shown in the photolysis of **1** in deuterated ACN.^[20] This implies that H⁺ formed in reaction (2) is consumed in the formation of salt **5**. In fact,



SCHEME 2 Proposed mechanism of ylide **1** photodecomposition and formation of phosphonium salts **5** and **9**

when the photolysis of **1** is carried out in ACN, the reaction mixture is neutral. When DCM is used as a solvent, the reaction mixture is acidified in the reaction course.^[21] This may imply that the acid is formed with participation of the solvent in the radical reactions under the action of light. As a result of the reaction sequence (1) to (4), radicals C⁺HCl₂ and C⁺H₂Cl from the solvent are generated, with the former radical being dominant. These radicals can either recombine or disproportionate, or participate in other radical reactions (Scheme 3, reaction (5))^[11,12] or in the reactions (6) and (7) with traces of water in the presence of oxygen. ^[13] Reaction (6) gives phosgene, which decomposes in the reaction with H₂O (reaction (7)) to afford HCl.

The formation of the Cl-containing products in the photolysis of 1 at different concentrations is another confirmation of the DCM participation in the photoinduced radical reactions. In fact, several Cl-containing products (9-11) satisfy to the molecular ion $C_{26}H_{21}ClOP^+$ with M^+/z 415.1013 (Scheme 4). Compound 9 is the product of reaction (4b) (Scheme 2). Compound 10 is formed after HCl addition to 1, and the molecular ion corresponding to this adduct (M^+/z 619.1006) was found in trace amounts (Figure S2A, inset). It should be pointed out that iodonium compounds under study are detected by ESI-MS mainly after decomposition with elimination of PhI. Compound **11** is the decomposition product of **10**. The formation of compounds similar to 10 and 11 was shown for S_N2 pathway for vinylic nucleophilic substitution reactions in alkylvinyl(phenyl)iodonium salts.^[2,25]

The formula $C_{27}H_{20}O_2Cl_2P^+$ for the molecular ion with M⁺/z 477.0561 allows for the proposal that this is compound **12** (Scheme 4) formed with the participation of phosgene. It is clear that the formation of chlorine-containing products **10** to **12** is the results of the reactions with HCl and phosgene formed from DCM. In the presence of an acid independent of its source, **1** is

$$\dot{C}HCl_2 \xrightarrow{h_V} \dot{C}Cl + HCl \qquad (5)$$

$$\dot{C}HCl_2 \xrightarrow{O_2} CHCl_2 \dot{O}_2 \longrightarrow \dot{O}H + COCl_2 \quad (6)$$

$$COCl_2 + H_2 O \longrightarrow CO_2 + 2HCl \qquad (7)$$





SCHEME 4 Plausible structures of Cl-containing products

protonated first at the oxygen atom (13) and then the anion interacts with the iodonium group (Scheme 5).^[25] Similar process was observed in acylation of the ylide with trifluoroacetic anhydride.^[26] The intermediate protonated dication 13 should be more photoactive than the parent ylide, and we propose that the formation of this intermediate provides the acceleration of the photolysis in the presence of an acid. Recently, it has been shown that addition of trifluoroacetic acid (TFA) to the reaction of ylide 1 with phenylacetylene decreases the induction time and slightly accelerates the rate after the induction time at the acid concentrations lower than the initial ylide concentration.^[21] At the higher concentrations of the acid, the yield of the target phosphinoline 3 decreases crucially. At the low concentrations of ylide 1, the addition of the TFA excess results in the formation of the adduct with TFA identified by ESI-MS. These results show that at low acid concentrations dication 13 is in equilibrium with ylide 1 and may accelerate the reaction under the action of light. With an increase in the acid concentration, products 10 and 11 are formed. The manuscript on the detailed study of the interaction of 1 with acids is preparing for publication.

The comparison of the reaction products formed in the photolysis of **1** at various concentrations shows that if in general the product compositions are similar (Figure 4), they have different product impact. From the point of view of participation of DCM in the reaction course, it is clear that at the low concentrations, the radical photoinduced decomposition of 1 initiates photochemical radical reactions (5) to (7) (Scheme 3) in DCM with formation of HCl and phosgene to afford products 10 to 12. The formation of 5 in this case occurs not only in reaction (4a) but predominantly via decomposition of 10 to 12 in the second step (Figure 1D). Certainly, these processes also have their impact in the photolysis at the high concentrations. However, it should be taken into account that when [1] > 0.01 mol/L, almost all of the light falling on a cell is absorbed by ylide 1 itself, and the photoinitiation of radical reactions in DCM is much lower. In this case, the main reactions of the solvent are described by Scheme 2. Nevertheless, the photolysis of the ylide is accelerated, and the acceleration is caused by the formation of HCl from the solvent.

The difference in the course of the photolysis at different ylide concentrations is accounted for by the formation



SCHEME 5 Reaction of ylide 1 with an acid

of relatively large submicroparticles of the ylide with spectral properties different from the white crystals in the solid state and from diluted solutions, which are colorless. In addition to the change in the reaction products, this results in the bathochromic shift of the boundary irradiation wavelength up to 450 nm.

We suppose that specific organization of the ylide in the DCM solutions at the high concentrations determines the difference between the regularities in the photolysis of 1 alone at different concentrations and in the mixtures with acetylenes. As mentioned above, the ylide solutions at the high concentrations are stable microheterogeneous systems with a mean particle size of 900 nm. The rough assessment of a number of the ylide molecules forming these aggregates shows that more than hundreds millions molecules constitute the particle. When the ylide molecule in a particle absorbs the light, the generated radicals either exit from the particle surface to the bulk solution and reactions (2) to (4) (Scheme 2) take place, or interact with the ylide molecules within the particle to give minor products. At the low concentrations, when the solution contains small ylide aggregates, the reaction occurs practically in the bulk solution giving almost the same products but in other ratios. In this case, the conjugated photoinduced chain reaction in DCM becomes important giving the enhanced concentrations of Cl-containing products.

The optimum condition for the annulation reaction with acetylenes is their 3-fold to 5-fold excess.^[21] The observed inhibition of the ylide photolysis in the presence of 2 implies that phenylacetylene molecules isolate ylide from the solvent forming a shell around the ylide particle because of the better solubility of 2 and the complex formation between the triple bond of phenylacetylene 2 and the iodonium group.^[21,27] Upon light absorption, the radicals generated from 1 interact first with 1 and 2 within the particle because of the close proximity of the reagents. The radical reactions in the particle suppress reactions with DCM and the formation of salt 5. In reaction (2) (Scheme 2) and in the reaction of λ^5 -phosphinoline **3** formation (Scheme 1), H⁺ is evolved providing the acid catalysis because of the formation of intermediate 13. The process is autocatalytic, because the higher concentration of H⁺, the higher the initiation and vice versa.^[21]

5 | CONCLUSIONS

In summary, DCM is not an inert solvent in the photolysis of mixed phosphonium-iodonium ylide, with the solvent effect being dependent on the ylide concentration. At the low ylide concentrations, DCM is subjected to the photoinduced radical reactions with formation of HCl and phosgene resulting in the appearance of Cl-

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containing products. As the concentration of the ylide increases up to 0.01 mol/L and higher, the major factor affecting the photolysis mechanism is self-assembling of the ylide molecules to give large stable aggregates in DCM. This decreases the role of radical reactions in DCM but gives rise to the radical reactions in organized aggregates of the ylide alone or in its mixtures with acetvlenes. The peculiarities of the reaction between vlides and acetylenes find their explanation on the assumption that the radical reactions primarily occur in the organized aggregates. We suppose that the results obtained in this study are of general significance, because in one form or another DCM can participate in photoinduced radical reactions of various solutes. And last, but not least. currently, reactions in supramolecular self-assembled as well as in nanocrystalline systems attract considerable interest.^[28] Two approaches are used in the examination of these systems: from solid to microheterogeneous systems and from intrinsic solutions to microheterogeneous systems. The formation and recombination of diarylmethyl radicals were shown in photolysis of nanocrystalline suspensions of the tetraarylacetone, with the generation of radical pair being even faster than in solution.^[28b] In the system under consideration, the process is more complex chemically, and the target synthesis of heterocyclic compounds occurs only in microheterogeneous system, and our study on the kinetics of product formation shows that concentrating of the reagents in aggregates, so-called micellar effect, is not the only reason for the observed regularities.

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