Photo-on-Demand *In Situ* Phosgenation Reactions That Cross Three Phases of a Heterogeneous Solution of Chloroform and Aqueous NaOH

Akihiko Tsuda,* Naoko Ozawa, Ryo Muranaka, Tomoya Kuwahara, Ayako Matsune, and Fengying Liang

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ABSTRACT: Here, we report a novel photo-on-demand *in situ* phosgenation reaction that crosses three phases of a heterogeneous solution of chloroform ($CHCl_3$) and aqueous NaOH containing an aryl alcohol or amine. This reaction system enables the safe, convenient, and inexpensive synthesis of carbonate esters, polycarbonates, and N-substituted ureas from aryl alcohols, aryl diols, and primary/secondary amines, respectively, on a practical scale and with good yield. The photochemical oxidation of $CHCl_3$ to phosgene ($COCl_2$) occurs upon irradiation with UV light from a low-pressure mercury lamp of both the gas and liquid phases of the reaction system under O_2 bubbling of the vigorously stirred sample solution. The following reaction mechanisms are suggested: The aryl alcohol reacts *in situ* with the generated $COCl_2$ at the interfaces of the organic/aqueous phases and aqueous/gas phases, in competition with the decomposition of $COCl_2$ due to hydrolysis. Nucleophilicity and hydrophilicity are enhanced by the formation of aryl alkoxide ion through the reaction with NaOH, whereas the reaction of amine proceeds through neutralization of the generated HCl by the aqueous NaOH.
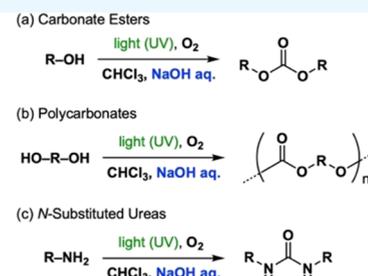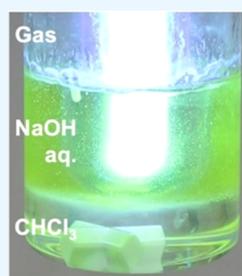
INTRODUCTION

Phosgene ($COCl_2$) is an industrially important C1 building block for synthesizing a variety of organic chemicals and polymers such as chloroformates, carbonate esters, N-substituted ureas, isocyanates, and polycarbonates (PCs).[1−5] It is a highly reactive compound for nucleophilic substitution reactions that provide carbonyl-containing products in high yield in a short time, with the elimination of HCl, which can be readily removed from the product and neutralized with an aqueous alkaline solution. For both chemical and economic reasons, the industrial production of $COCl_2$ continues to increase worldwide. However, since phosgene is extremely toxic, a variety of chemical reactions and processes that do not require phosgene, and reaction systems that enable safe phosgenation reactions, have been developed.[6−8]

Phosgene is mainly supplied using the following on-demand production methods: (1) chemical reaction of CO and Cl_2 with a carbon catalyst[9] and (2) decomposition of bis-(trichloromethyl)carbonate and trichloromethyl chloroformate, so-called triphosgene and diphosgene, respectively, with an organic base.[8,10] Method (1) enables the continuous production of $COCl_2$ by careful handling of the exothermal reaction of CO and Cl_2, although both compounds are highly toxic, by using a special apparatus to provide a safe system. Method (2) allows the *in situ* generation of $COCl_2$ but is limited to phosgenation reactions that proceed in the presence of an organic base. The former and latter methods are

preferably used for large-scale and small-scale syntheses, respectively, upon consideration of the overall benefits of each approach, such as safety, cost, amount, apparatuses, and environmental impacts.

Interfacial polycondensation reaction of bisphenol A (BPA) or its derivatives with $COCl_2$ in a heterogeneous solution of dichloromethane (CH_2Cl_2) and aqueous NaOH is a major method for synthesizing PCs in industry [Scheme 1, reaction (a)].[11] The continuous supply of $COCl_2$, which requires careful handling, into the reaction system, is a key process for safe syntheses. Further, a patent application reported the synthesis of diphenyl carbonate (DPC) by direct addition of $COCl_2$ into an aqueous alkaline solution containing phenol [Scheme 1, reaction (b)].[12] Since $COCl_2$ does not undergo rapid hydrolysis when mixed with water or alkaline water, interfacial phosgenation reactions may be possible. The inorganic base promotes competitive condensation reactions of $COCl_2$ with both alcohol and water. This method is preferred for industrial large-scale synthesis but is not suitable for the relatively small-scale synthesis of a variety of organic

Scheme 1. Conventional Phosgenation Reactions in the Synthesis of (a) PC and (b) DPC with Aqueous NaOH, and Photo-on-Demand *In Situ* Phosgenation Reactions with (c) Organic Base and (d) NaOH aq

I. Conventional Phosgenations with NaOH aq.

(a)   HO–R–OH + COCl$_2$ $\xrightarrow[\text{NaOH aq.}]{\text{CH}_2\text{Cl}_2}$ PC

(bisphenol)

(b)   PhOH + COCl$_2$ $\xrightarrow{\text{NaOH aq.}}$ DPC (PhO–CO–OPh)
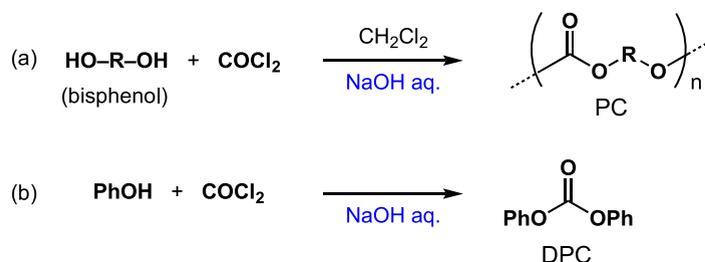
II. [Previous Work]
Photo-on-demand Phosgenation with a Homogeneous Solution

(c)   NuH + CHCl$_3$ + O$_2$ $\xrightarrow[\text{org. base}]{\text{light (UV)}}$ Nu–CO–Nu
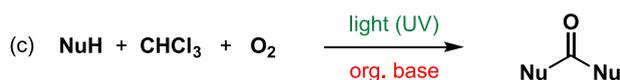
III. [This Work]
Photo-on-demand Phosgenation with a Heterogeneous Solution

(d)   NuH + CHCl$_3$ + O$_2$ $\xrightarrow[\text{NaOH aq.}]{\text{light (UV)}}$ Nu–CO–Nu
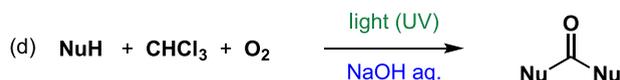
NuH: R–OH or R–NH$_2$

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chemicals such as pharmaceutical intermediates. Given this background, we were motivated to develop a safer, more convenient, and less expensive phosgenation reaction that allows the on-demand and on-site versatile synthesis of organic chemicals on variable scales.

In a pioneering study, we reported the photo-on-demand synthesis of COCl$_2$ from CHCl$_3$.[13] The reaction occurred efficiently in a short time upon irradiation of CHCl$_3$ under O$_2$ bubbling using UV-C light from a low-pressure mercury lamp (LPML). We then developed photo-on-demand *in situ* phosgenation reactions for synthesizing a variety of organic chemicals and polymers with CHCl$_3$ solutions containing both a substrate and an organic base [Scheme 1, reaction (c)].[14−21] Although alcohols such as EtOH serve to stabilize CHCl$_3$, and the organic bases and solvents absorb UV-C light,[22,23] the phosgenation products were obtained in high yields through *in situ* reactions of the substrates and COCl$_2$ generated from CHCl$_3$. These results indicated that the photochemical oxidation of CHCl$_3$ occurred not only in the liquid phase but also in the gas phase. In support of this hypothesis, we recently reported that gaseous CHCl$_3$ underwent efficient photochemical oxidation to give COCl$_2$ in >96% yield.[24] We expected that the photochemical oxidation of CHCl$_3$ would occur in the gas phase even with a heterogeneous mixture of CHCl$_3$ and water, given the large difference in their vapor pressures (21.1 and 2.3 kPa, respectively, at 20 °C).[25] In this study, we report the first example of photo-on-demand *in situ* phosgenation reactions promoted by an inorganic base with heterogeneous mixtures of CHCl$_3$ and aqueous alkaline solution containing an aryl alcohol or amine [Scheme 1, reaction (d)]. We show that this reaction is applicable to the

synthesis of carbonate esters, polycarbonates, and N-substituted ureas.[18]

RESULTS AND DISCUSSION

Experimental Setup for *In Situ* Photo-on-Demand Phosgenation Reactions with an Aqueous Inorganic Base Solution. A low-pressure mercury lamp generates UV-C light, mainly with wavelengths of 184.9 and 253.7 nm. This UV-C light brings about $\sigma−\sigma^*$ and/or $n−\sigma^*$ transitions in CHCl$_3$.[16,26] The photochemical oxidation of CHCl$_3$ can proceed *via* a radical chain mechanism. The exposure of CHCl$_3$ to UV-C light results in C−Cl bond breakage to generate Cl$^\bullet$, which extracts hydrogen from another CHCl$_3$ to produce Cl$_3$C$^\bullet$ (trichloromethyl radical). This radical then reacts with O$_2$ to give COCl$_2$ and the regeneration of Cl$^\bullet$, allowing repetition of the reaction. The lamp (20 W, ø24 mm × 120 mm, illuminance at distances of 5 mm: 2.00−2.33 and 5.96−8.09 mW/cm^2 at 185 and 254 nm, respectively) was inserted into the sample solution *via* a quartz glass jacket (ø28 mm × 150 mm) at the center of a cylindrical flask (ø42 mm × 170 mm) (Figure 1). Scale-up synthesis was achieved by changing the size of the cylindrical flask (ø60 mm × 170 mm). A cooling condenser to liquefy vapors such as COCl$_2$ and CHCl$_3$ was attached to the cylindrical flask. The reactions were conducted with a heterogeneous solution of CHCl$_3$ and aqueous NaOH containing a reaction substrate. Oxygen gas (90% concentration) generated by an O$_2$ generator was introduced into the CHCl$_3$ phase (bottom) *via* a PTFE tube (outer and inner diameters: ø3 and 2 mm, respectively) by controlling the flow rate with a mass flow controller. The sample solution was vigorously stirred by a cross-shaped

Figure 1. Experimental setup for photo-on-demand *in situ* phosgenation reactions with a heterogeneous mixture of $CHCl_3$ and aqueous NaOH.

magnetic stirring bar (diameter and height: ø25 mm × 8 mm) using a magnetic stirrer set at the maximum speed of rotation.

Optimization of the Synthesis of Carbonate Esters. A preliminary experiment using the above reaction system revealed that $CHCl_3$ photo-decomposed upon exposure to UV light under O_2 bubbling in the presence of a phase-separated aqueous NaOH solution. The $COCl_2$ generated from $CHCl_3$ could potentially undergo hydrolysis to give CO_2 and HCl. We examined the photochemical synthesis of a carbonate ester. The UV light was shone onto a mixture of $CHCl_3$ (20 mL, 250 mmol) and aqueous solution (20 mL) containing an alcohol (10–30 mmol) and NaOH (100 mmol) or Na_2CO_3 (40 mmol), with O_2 bubbling (0.1 L/min) at 20 °C for 3–5 h or 0 °C for 6 h under vigorous stirring (Table 1). The reaction was stopped before complete consumption of the base. The desired reaction occurred using 10 mmol of phenol at 20 °C for 3 h and provided diphenyl carbonate (DPC) in 55% yield (entry 1), where exhaust $COCl_2$ gas was converted to the alkyl carbonate (61 mmol) in the butanol trap attached. ^{1}H NMR spectroscopic analysis revealed that the remaining water phase contained the unreacted phenol (43%). The yield of DPC decreased to 47% by lengthening the reaction time,

probably due to photo-decomposition of the product (entry 2). Tripling the amount of substrate approximately doubled the total amount of the product, but the yield decreased to 33% (entry 3). The reaction was decelerated by decreasing the temperature to 0 °C to attain a 32% yield after 6 h (entry 4). No product was obtained using an aqueous Na_2CO_3 solution (entry 5) or with water without a base (entry 6). Ethanol, a lower alkyl alcohol, provided no notable product both in reactions with or without NaOH (entries 7 and 8, respectively). Interestingly, however, 1-hexanol, which is less volatile than EtOH, provided the corresponding carbonate in 6% yield with NaOH aq, or a mixture of chloroformate and the carbonate in 84 and 6% yields, respectively, with water (entries 9 and 10, respectively).

Reaction Mechanism with Alcohols. The observed differences of the products obtained by the reactions of EtOH and 1-HexOH indicated that EtOH dramatically decelerated the photochemical oxidation of $CHCl_3$ in both the gas and liquid phases, while 1-HexOH, which is less volatile than EtOH, allows the reaction in the gas phase (Table 1, entries 7–10). The generated $COCl_2$ immediately reacts with 1-HexOH to give chloroformate **2**, which then slowly reacts with the remaining 1-HexOH to give carbonate **1** in entry 10. However, the hydrolysis of **2** can be accelerated by aqueous NaOH to regenerate 1-HexOH and generate CO_2 in entry 9. Therefore, the alcohol dissolved in the solution might react with $COCl_2$ generated mainly from the gas phase (Figure 2).[24] Given that the alkyl alcohol provided no or little product in entries 7 and 9, whereas PhOH, an aryl alcohol, provided the corresponding carbonate (DPC) in ~55% yield in entry 1, the condensation reaction of alcohol and $COCl_2$ can be accelerated by the formation of sodium phenoxide, which is generally more stable than alkyl alkoxides. This condensation reaction enhances both the nucleophilicity and hydrophilicity of the alcohol, and consequently, the reactions may occur dominantly around the interfaces of the organic/aqueous and aqueous/gas phases (reactions 1–4). The produced carbonate ester also undergoes hydrolysis to reproduce the alcohol substrates, together with the generation of CO_2 (reaction 5). In summary, the yield of carbonate ester produced ultimately in the organic phase is dependent on several factors, as follows:

Table 1. Photochemical Synthesis of Carbonate Esters from Alcohols with $CHCl_3$ and an Aqueous Inorganic Base Solution[a]

$$R{-}OH \ + \ CHCl_3 \ (20\ mL) \xrightarrow[\text{water (20 mL), base, } T\ (°C),\ \text{time}]{\text{light (UV), } O_2} \underset{\mathbf{1}}{R_O \overset{O}{\underset{}{\|}} O_R} \ + \ \underset{\mathbf{2}}{R_O \overset{O}{\underset{}{\|}} Cl}$$

	ROH (mmol)		base (mmol)				yield (%)[b]	
entry					T (°C)	time (h)	**1**	**2**
1	PhOH	10	NaOH	100	20	3	55	n.d.
2	PhOH	10	NaOH	100	20	5	47	n.d.
3	PhOH	30	NaOH	100	20	3	33	n.d.
4	PhOH	30	NaOH	100	0	6	32	n.d.
5	PhOH	10	Na_2CO_3	40	20	3	n.d.	n.d.
6	PhOH	10			20	3	n.d.	n.d.
7	EtOH	10	NaOH	100	20	3	n.d.	n.d.
8	EtOH	10			20	3	n.d.	n.d.
9	1-HexOH	10	NaOH	100	20	3	6	n.d.
10	1-HexOH	10			20	3	6	84

[a]Reaction procedures and conditions: irradiation of the sample solution under O_2 bubbling (0.1 L/min) by UV light from a 20 W low-pressure mercury lamp. [b]Yields were determined by ^{1}H NMR analysis. n.d.: not detected.

Figure 2. Proposed mechanism for the photochemical interfacial synthesis of a carbonate ester with an alcohol in a heterogeneous mixture of CHCl$_3$ and aqueous NaOH solution.

(a) the volatility of the alcohol affects the efficiency of the photochemical oxidation of CHCl$_3$, (b) product stability, due to the electrophilicity of the carbonyl group and the ease of elimination of the substituent groups, (c) the solubilities of the substrate and product in the organic and aqueous phases, and (d) the equilibrium between the alcohol and alkoxide ion in the reaction with NaOH.

In contrast, CHCl$_3$ provides dichlorocarbene (CCl$_2$) through the reaction with strong bases such as NaOH. CCl$_2$ is highly reactive and causes the Reimer–Tiemann reaction with phenol, giving a mixture of o- and p-hydroxybenzaldehydes.[27] However, none of these possible compounds were observed in the sample solution after the reaction. As a reference experiment, when a CHCl$_3$/NaOH aq solution containing cyclohexene, which can form gem-dichlorocyclopropane through [1 + 2]cycloaddition with CCl$_2$,[28] was stirred for 3 h at 20 °C, no product was observed by ^{1}H NMR analysis in the resulting sample solution (Scheme 2a). However, the

Scheme 2. Reference Experiments to Trap Carbene Formed upon Mixing CHCl$_3$ and an Aqueous NaOH Solution
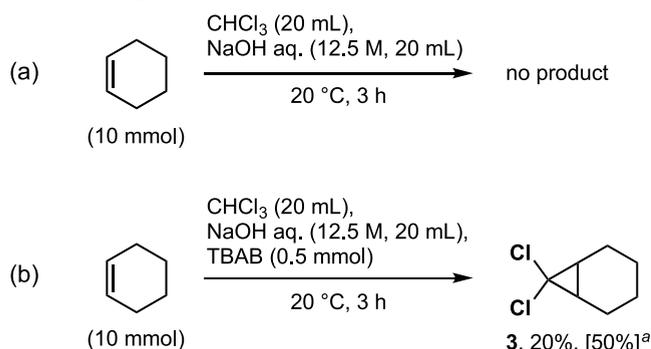
^{a}Isolated yield is given with the ^{1}H NMR yield in brackets (vs cyclohexene). TBAB: tetrabutylammonium bromide.

expected product **3** was obtained in 20% yield through the reaction in the presence of tetrabutylammonium bromide (TBAB), which serves as a phase-transfer catalyst (Scheme 2b). As an additional reference experiment, when cyclohexene was added to the reaction to synthesize DPC under the same conditions as in entry 1 of Table 1, **3** was not detected by ^{1}H NMR analysis. These results suggest that no special treatment is required to inactivate the possible carbene using the reaction conditions described above.

Synthesis of Substituted Aryl Carbonates. We next demonstrated reactions with substituted phenols. 4-*tert*-butylphenol, whose alkyl group likely increases the solubility of both the substrate and product in the organic phase, provided the corresponding carbonate **4a** in 47% yield (Scheme 3), which is rather lower than that obtained using phenol (Table 1, entry 1). 4-Methoxyphenol containing electron-donating groups provided **4b** in higher 60% yield. The phosgenation reaction enables synthesis of carbonate esters bearing electron-withdrawing substituent groups, which are hardly synthesized by the non-phosgenation methods. 4-Nitrophenol containing electron-withdrawing groups provided the corresponding carbonates **4c** in lower (5%) yield. The dramatic decrease in the yield of **4c** can be ascribed to the lower nucleophilicity of 4-nitrophenol compared to that of DPC in entry 1 of Table 1. 4-Fluorophenol has an electron-withdrawing F group and provided **4d** in 37% yield, which is lower than the yield of DPC but higher than the yield of **4c**. However, 3,4,5-trifluorophenol and pentafluorophenol provided the corresponding carbonates **4e** and **4f** in higher (87%) and comparable (55%) yields, respectively, since multi-fluorinated compounds generally have low affinities with conventional organic solvents and water, and thus can self-assemble to form bulk aggregates, resulting in their segregation from the sample solution.

Synthesis of Polycarbonates. We next examined the photo-on-demand *in situ* interfacial synthesis of polycarbonates (PCs) with bisphenol A (BPA) and its derivatives in a heterogeneous solution of CHCl$_3$ and aqueous NaOH. For more practical scale synthesis, the cylindrical flask was replaced with a larger flask (ø60 mm × 170 mm), and the reaction conditions were optimized. When the UV light was shone onto a mixture of CHCl$_3$ (90 mL) and aqueous NaOH solution (40 mL, 1.2 M) containing BPA (10 mmol) with O$_2$ bubbling (0.1 L/min) at 20 °C for 4 h under vigorous stirring, the corresponding polycarbonate BPA-PC was obtained in 79% yield with an average molecular weight of M_w = 34 000, M_n = 12 000, and PDI = 2.83 [Scheme 4, reaction (a)]. BPA derivatives, bearing cyclohexyl or cyclododecyl rings (BPZ and BPCD, respectively), are more lipophilic than BPA and provided the corresponding PCs in 88 and >99% yields, respectively, with average molecular weights of M_w = 8800, M_n = 2800, PDI = 3.15 and M_w = 16100, M_n = 7000, PDI = 2.30, respectively [reactions (b) and (c), respectively]. Bisphenol AF, bearing electron-withdrawing CF$_3$ groups, provided the corresponding PC with smaller average molecular weights of M_w = 16 000, M_n = 4900, and PDI = 3.27 [reaction (d)]. The degree of polymerization is most likely dependent on the nucleophilicity of the diol and the solubility of the substrate

Scheme 3. Photochemical Synthesis of Carbonate Esters from Substituted Aryl Alcohols with $CHCl_3$ and an Aqueous NaOH Solution[a]
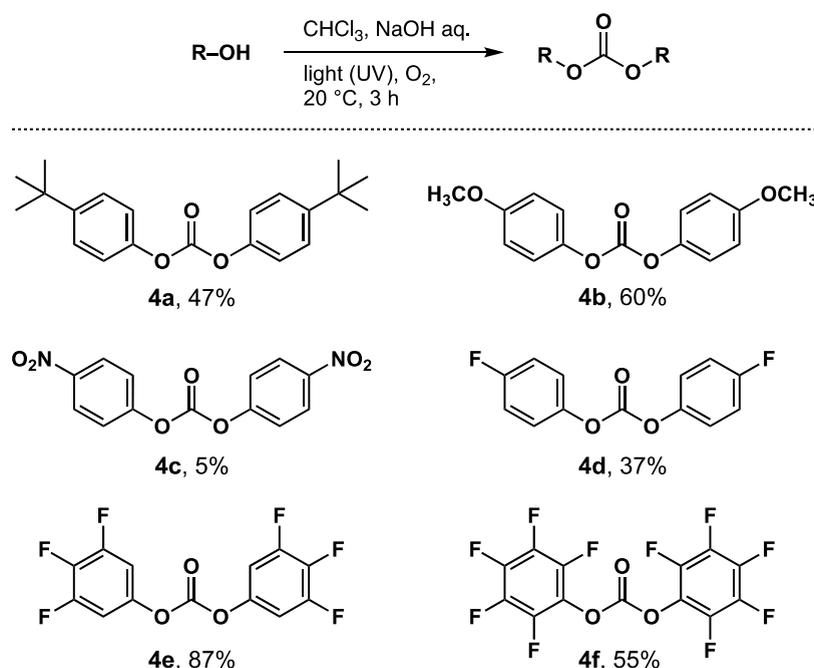
[a]Reaction procedures and conditions: irradiation by UV light from a 20 W low-pressure mercury lamp of a mixture of alcohol (10 mmol), $CHCl_3$ (20 mL), and aqueous NaOH solution (20 mL, 5 M) under O_2 bubbling (0.1 L/min) at 20 °C for 3 h. Isolated yields are given.

and product in the heterogeneous mixture solution comprising $CHCl_3$ and aqueous NaOH.

Synthesis of N-Substituted Ureas. The phosgenation reaction with a heterogeneous solution of $CHCl_3$ and NaOH aq was also available for the synthesis of N-substituted ureas from amines, which are more basic than alcohols. Aniline, an aromatic amine, provided the corresponding urea **5a** only in 12% yield (Scheme 5), which was clearly lower than the yield obtained in the synthesis of DPC from phenol (Table 1, entry 1). However, a series of primary alkyl amines such as hexylamine, benzylamine, and cyclohexylamine provided the corresponding ureas **5b**, **5c**, and **5d** in higher (51, 65, and 65%) yields, respectively. The reaction also proceeded with the HCl salt of an amine. For example, use of the ethylamine HCl salt gave 1,3-diethylurea **5e** in 14% yield. This low yield was likely due to the low boiling point of ethylamine (16.6 °C) formed by the reaction with NaOH. Further, piperidine, a secondary amine, provided the corresponding urea **5f** in 38% yield. These results suggest a non-interfacial reaction mechanism: The aqueous NaOH solution neutralizes the generated HCl, which decelerates the nucleophilic substitutions of amines to $COCl_2$ by forming the ammonium salt in the organic phase.

CONCLUSIONS

In this study, we developed photo-on-demand *in situ* phosgenation reactions that cross three phases comprising a heterogeneous solution of $CHCl_3$ and an aqueous NaOH solution containing an alcohol or amine. This new method enabled the synthesis of a variety of valuable organic compounds such as carbonate esters, polycarbonates, and N-substituted ureas. Photochemical oxidation of $CHCl_3$ to $COCl_2$ occurred upon irradiation with UV light from a low-pressure mercury lamp of gas and liquid phases of the reaction

system under O_2 bubbling of the sample solution with vigorous stirring. The reaction mechanism for aryl alcohols and amines is likely different due to differences in their solubility in aqueous NaOH. Aryl alcohols react with the generated $COCl_2$ *in situ* at the interface between $CHCl_3$ and NaOH aq, in competition with the decomposition of $COCl_2$ due to hydrolysis. The aryl alcohol enhances nucleophilicity and hydrophilicity by the formation of an aryl alkoxide ion through a reaction with NaOH to accelerate the condensation reaction. Reactions with amines to give N-substituted ureas might be accelerated through neutralization of the generated HCl by aqueous NaOH. These reactions can be conducted under light-control, allowing safe and convenient phosgenation reactions. Our proposed approach will benefit the relatively small-scale production of a wide variety of organic chemicals and polymers in both industry and academia.

EXPERIMENTAL SECTION

Materials and Instrumentation. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. The photoreactor consisted of a cylindrical flask (ø42 or 60 mm × 170 mm) containing a cross-shaped magnetic stirring bar (ø25 mm × 8 mm), a quartz glass jacket (ø28 mm × 150 mm), a cooling condenser (0 °C), a low-pressure mercury lamp (SEN Light Co., UVL20PH-6, 20 W, ø24 mm × 120 mm), and a magnetic stirrer (Technoapplications Co., Ltd. Magnetic Tornador PM-2000). Oxygen gas (concentration: 90%) was produced by an oxygen generator (GL Sciences Inc. OM-904C), and its flow rate was controlled by a mass flow controller (KOFLOC Co., Ltd. EX-250SC-RJ-24-V-V). The exhaust gas was washed using a double trap system with methanol and saturated aqueous $NaHCO_3$. The photoreactor, oxygen generator, and gas-scrubbing systems were connected by PTFE tubes with

Scheme 4. Photochemical Interfacial Synthesis of Polycarbonates from BPA and Its Derivatives with CHCl₃ and an Aqueous NaOH Solution[a]
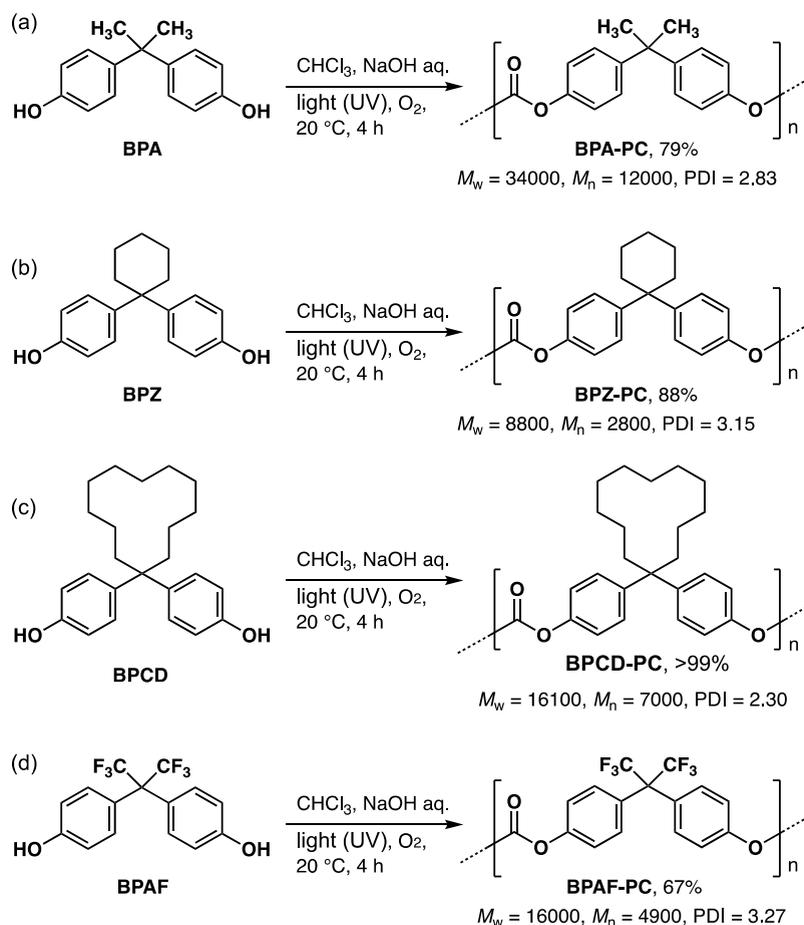
[a]Reaction procedures and conditions: irradiation by UV light at 20 °C for 4 h with a 20 W low-pressure mercury lamp of a mixture of diol (10 mmol), CHCl₃ (90 or 40 mL), and aqueous NaOH solution (40 mL, 1.2 M or 50 mL, 4.0 M) under O₂ bubbling (0.1 L/min). Isolated yields are given.

inner and outer diameters of ø2 and 3 mm, respectively. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethyl silane (TMS) as an internal standard. The illuminances of 185 and 254 nm light were recorded on a UV power meter composed of a controller (Hamamatsu Photonics K.K., model C9536) and a sensor head (model H9535-185 or H9535-254). For vacuum distillation, a glass tube oven (Sibata Scientific Technology, model GTO-1000) was used with an oil rotary vacuum pump or a diaphragm pump. Gel permeation chromatography (GPC) was performed at 40 °C on a JASCO LC-2000 HPLC system with Tosoh TSKgelG5000H$_{HR}$, TSKgelG4000H$_{HR}$, and TSKgel guardcolumnH$_{HR}$-H columns using a JASCO Type PU-2089 quaternary gradient pump, coupled with a JASCO MD-2018 Plus photodiode array (PDA) detector and a JASCO Type RI-4030 refractive index detector with THF as the eluent at a flow rate of 1.0 mL/min. Polystyrene standard samples (427 000, 123 000, 50 000, 13 502, 4000 Da) were used to calibrate the molecular weights of the polymers.

General Procedure for the Synthesis of Carbonate Esters. A cylindrical flask (ø42 mm × 170 mm) was charged with a mixture of CHCl₃ (20 mL), aqueous NaOH solution (20 mL, 5 M), and an alcohol substrate (10 mmol). A water

bath was used to keep the temperature of the sample solution at 20 °C. The sample solution was vigorously stirred during exposure to the UV light with O₂ bubbling (0.1 L/min) for 3 h. The resulting sample solution was washed with water and extracted with CHCl₃ or CH₂Cl₂. The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was dried under vacuum at 30−70 °C for 1−2 h, and if necessary, recrystallized from CH₂Cl₂/n-hexane or CHCl₃/MeOH, or vacuum-distilled using a glass tube oven to give the corresponding carbonate ester.

General Procedure for the Synthesis of Polycarbonates. A cylindrical flask (ø60 mm × 170 mm) was charged with a mixture of CHCl₃ (90 or 40 mL), aqueous NaOH solution (1.2 M/40 mL or 4.0 M/50 mL), and a diol (10 mmol). A water bath was used to keep the temperature of the sample solution at 20 °C. The sample solution was vigorously stirred during exposure to the UV light with O₂ bubbling (0.1 L/min) for 4 h. The resulting sample solution was washed with water and extracted with CHCl₃ or CH₂Cl₂. The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was dried under vacuum at 30−70 °C for 1−2 h and reprecipitated from CH₂Cl₂ and MeOH to give the corresponding polycarbonate.

Scheme 5. Photochemical Synthesis of N-Substituted Ureas from Amines with CHCl₃ and an Aqueous NaOH Solution[a]

$$R-NH_2 \quad \xrightarrow[\substack{\text{light (UV), O}_2, \\ 10-20\,°C, \, 2-5\,h}]{\text{CHCl}_3, \text{NaOH aq.}} \quad R\underset{H}{\overset{O}{\underset{N}{\parallel}}} \overset{}{\underset{H}{N}}R$$
(or R–NH₃⁺Cl⁻)

5a, 12%   **5b**, 51%

5c, 65%   **5d**, 65%

5e, 14%   **5f**, 38%
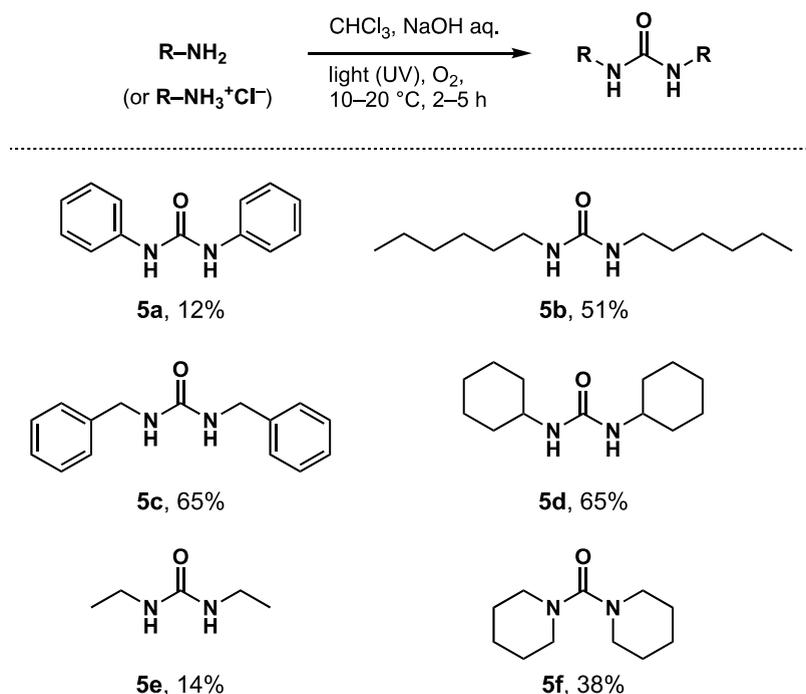
[a]Reaction procedures and conditions: irradiation by UV light at 10 or 20 °C for 2–5 h with a 20 W low-pressure mercury lamp of a mixture of amine or HCl salt of amine (10 mmol), CHCl₃ (20 mL), and aqueous NaOH solution (20 mL, 5 M) under O₂ bubbling (0.1 L/min). Isolated yields are given.

General Procedure for the Synthesis of N-Substituted Ureas. A cylindrical flask (ø42 mm × 120 mm) was charged with a mixture of CHCl₃ (20 mL), aqueous NaOH solution (20 mL, 5 M), and an amine substrate (10 mmol). A water bath was used to keep the temperature of the sample solution at 20 °C. The sample solution was vigorously stirred under exposure to UV light with O₂ bubbling (0.1 L/min) for 3 h and then washed with water and extracted with CHCl₃ or CH₂Cl₂. The combined organic layer was dried over anhydrous Na₂SO₄ and evaporated to dryness. The residue was dried under vacuum at 70 °C for 2 h and, if necessary, recrystallized from CH₂Cl₂/n-hexane or subjected to silica gel column chromatography with CH₂Cl₂ as an eluent to give the corresponding N-substituted urea.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c04290.

Experimental procedures, copies of ¹H, ¹³C{¹H}, and ¹⁹F NMR spectra, and GPC profiles (PDF)

AUTHOR INFORMATION

Corresponding Author

Akihiko Tsuda − *Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan;* orcid.org/0000-0002-9232-1455; Email: tsuda@harbor.kobe-u.ac.jp

Authors

Naoko Ozawa − *Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan*

Ryo Muranaka − *Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan*

Tomoya Kuwahara − *Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan*

Ayako Matsune − *Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan*

Fengying Liang − *Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501, Japan*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.3c04290

Notes

The authors declare no competing financial interest.

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