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FOCUS REVIEW

In situ photo-on-demand phosgenation reactions with chloroform for syntheses of polycarbonates and polyurethanes

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Abstract

Phosgene is an important carbonyl source for industrial production of polycarbonates (PCs) and polyurethanes (PUs). However, since it is highly toxic, alternative compounds and/or new phosgenation reactions have been explored for safety reasons. Given this background, we found a novel photochemical reaction enabling the synthesis of phosgene from chloroform. Subsequently, we developed new phosgenation reactions and reaction systems, and the key objective was “safe application” to organic synthesis. This focus review reports our recent use of in situ photo-on-demand phosgenations of alcohols and amines in synthesizing PC, PU, and their precursors, such as chloroformates, carbonate esters, and diisocyanates, in batch reaction systems, which are preferable for laboratory or small-scale industrial syntheses. We believe that the present reactions have advantages over conventional phosgenation reactions, especially in terms of safety and environmental impacts, and are expected to make positive contributions to practical organic syntheses in both academia and industry.

Introduction

Phosgene has the chemical formula $COCl_2$, is an important C1 building block in organic synthesis and is used as a raw material for the syntheses of polycarbonates (PCs) and polyurethanes (PUs) [1–10]. However, its laboratory use is often restricted due to its extremely high toxicity [11]. Industrially, it is used in large quantities worldwide with strict legal controls of (1) the storage and transport of phosgene; (2) the use of large quantities of toxic substances (gases) as raw materials; and (3) the disposal of waste, including chlorinated byproducts. The global market for phosgene has grown continuously with the increased production of PCs and diisocyanates such as toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI), which are precursors in the production of PUs [4–10], along with the production of pharmaceuticals, pesticides, and dyes. Phosgene is generally manufactured on-site and on-demand, where and when it is needed, and only in the quantities needed. Currently, in large-scale industrial processes, it is produced from carbon monoxide (CO) and chlorine (Cl_2) gas at 50–150 °C with a carbon catalyst [Fig. 1, reaction (a)] [12, 13]. This method of production has remained essentially unchanged since approximately 1920 and is now an established method for phosgene production [2]. However, the method has clear associated safety risks due to the high toxicity of CO and the toxicity/corrosiveness of Cl_2, and their intense exothermic reaction requires temperature control. Furthermore, given global climate change and the consequent strong demand and need for carbon neutrality, innovative phosgene production methods have attracted social attention [14].

To reduce the safety risk, in situ production of phosgene via decomposition of triphosgene (BTC), which is a solid at room temperature and soluble in organic solvents, with organic bases [Fig. 1, reaction (b)] is mainly used for relatively small-scale chemical syntheses in both academia and industry [15–17]. However, Cotarca and coworkers recently reported on the risks of BTC, which also has high toxicity and easily reaches toxic concentrations due to its high vapor pressure, and warned against unrestricted use [18]. Furthermore, the use of organic bases in BTC phosgenation reactions produces the hydrochloride salt in solution owing to the presence of HCl generated from the reaction of phosgene and the substrate. This can lead to

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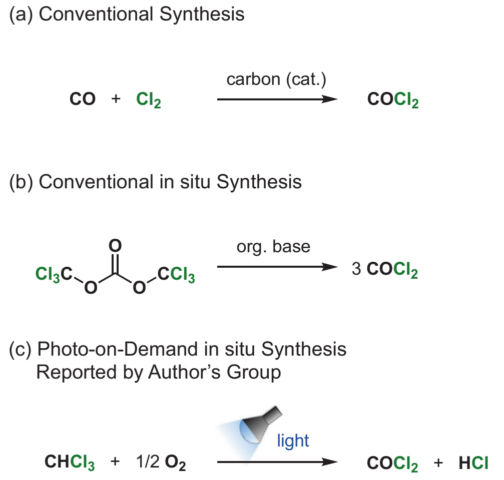


Fig. 1 Conventional phosgene syntheses with (a) CO/Cl_2 and (b) triphosgene and (c) novel photo-on-demand syntheses with chloroform

mechanical system issues, such as difficulty in stirring the batch tanks and clogging the flow systems. Furthermore, the hydrochloride salt generated in the reaction must be removed through an additional purification process. Although alterations to conventional phosgene syntheses and alternative nonphosgene methods have been studied [19, 20], they have only marginally replaced the current methods due to their higher costs and higher environmental impacts.

In light of this, we developed a photo-on-demand synthesis of phosgene from chloroform ($CHCl_3$) [Fig. 1, reaction (c)] [21, 22]. The photochemical oxidation of $CHCl_3$ to $COCl_2$ occurs efficiently upon irradiation with a 20 W low-pressure mercury lamp (LPML), which emits 184.9 and 253.7 nm UV light, with O_2 bubbling at room temperature. In the early stage of this study, we synthesized a variety of organic chemicals, including polymers, with the gaseous photooxidation products of $CHCl_3$ by using a gas-transport reaction system (Fig. 2, system [I]) [23, 24]. However, this reaction system had a potential risk of leakage, such as the case of reaction (a) in Fig. 1. To ensure safe use of this reaction, we then developed "in situ" photo-on-demand phosgenation reactions, which required the design and construction of batch and flow reaction systems [25–34]. We have successfully applied this photo-on-demand phosgenation reaction on a practical scale for most common phosgenation reactions, such as the syntheses of chloroformates [25, 26], carbonate esters [28, 29], PCs [28], isocyanates [30], Vilsmeier reagents [27], acyl chlorides [25], and *α*-amino acid *N*-carboxyanhydrides (NCAs) [32] (Fig. 3). This review article highlights the reactions of alcohols and amines used in synthesizing PC, PU, and their precursors, and the examples are limited to those using the batch reaction system. These reactions have the potential to replace the conventional reactions and exhibit superior safety and low energy consumption; additionally, chloroform is a common organic solvent and is readily available as a raw material for a wide variety of reactions conducted on various scales.

Mechanism for the photochemical oxidation of $CHCl_3$

The photochemical oxidation of $CHCl_3$ may proceed through a radical chain mechanism initiated by photolytic cleavage of a C–Cl bond [path (a) in Fig. 4]. The eliminated $Cl^•$ reacts with $CHCl_3$ to give $Cl_3C^•$ and HCl. The resulting $Cl_3C^•$ initiates a radical chain reaction with O_2 to give $COCl_2$ with elimination of a $Cl^•$ [path (b) in Fig. 4] [22, 35]. This reaction mechanism was supported by the observation that the yield of the byproduct hexachloroethane (C_2Cl_6) increased with decreasing oxygen concentrations in the reaction system. It is also known that $COCl_2$ decomposes under UV irradiation to give CO, CO_2, and Cl_2. The generated Cl_2 most likely served as an additional source of $Cl^•$, which accelerated the photochemical oxidation of $CHCl_3$. In general, alcohols such as ethanol are used as stabilizers to inhibit the decomposition of $CHCl_3$ [36] and may serve as radical scavengers to regenerate $CHCl_3$ from the halomethane radicals. However, when the concentration of the halomethane radicals exceeded the threshold alcohol concentrations in both the liquid and vapor phases, the photooxidation of $CHCl_3$ supported phosgenation of the alcohol. This enabled the development of the in situ photo-on-demand phosgenation reactions described in this review article.

Experimental setup of a batch-type photoreaction system

Low-pressure mercury lamps generally exhibit low electric power consumption and generate UV light with wavelengths of 184.9 and 253.7 nm, which match the electronic absorption bands of $CHCl_3$ arising from σ–σ* and/or n–σ* transitions [37]. The lamp (20 W, ø24 mm × 120 mm) exhibited a 254 nm illuminance of 6.2–9.0 mW/cm^2 at 5 mm from the lamp and was inserted into the $CHCl_3$ solution in a quartz glass jacket (ø28 mm × 150 mm) fixed in the center of a cylindrical flask (ø42 mm × 170 mm) equipped with an alcohol/water-cooled condenser (Fig. 2, system [II]). The photochemical reactions were conducted in this reaction system while a steady flow of O_2 (0.1–0.5 L/min) was bubbled through $CHCl_3$ with or without the substrate for the phosgenation reaction and with stirring of the sample solution at various temperatures. The reactions were demonstrated with a closed system, but the exhausted gas containing unreacted $COCl_2$ and the generated HCl

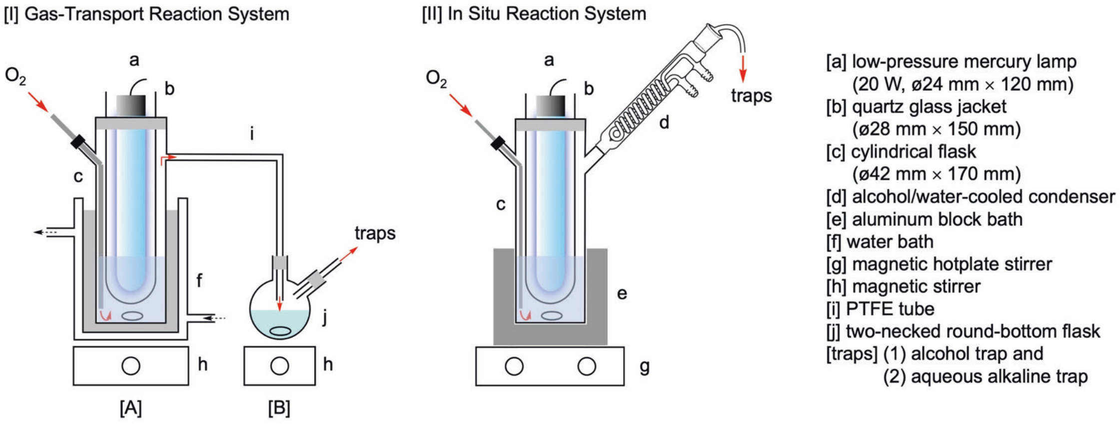


Fig. 2 Schematic illustration of the experimental setup for the photo-on-demand phosgenation reactions: [I] gas-transport reaction system and [II] in situ reaction system

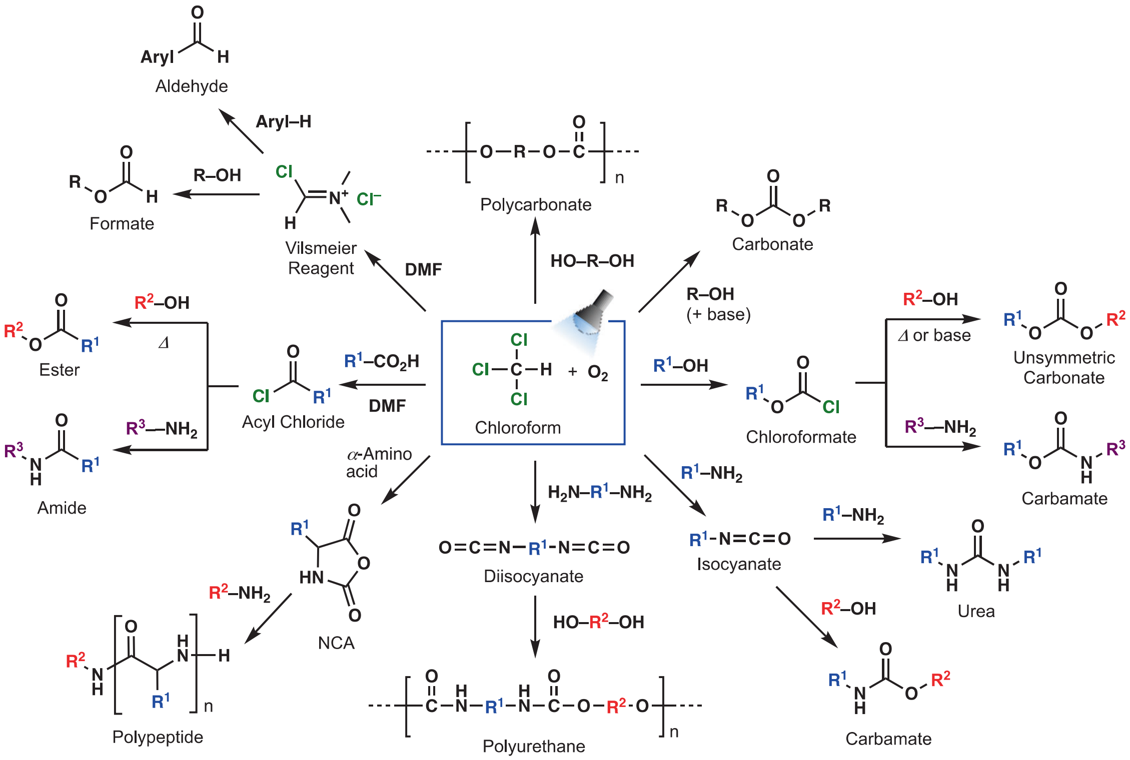


Fig. 3 In situ photo-on-demand phosgenation reactions with $CHCl_3$ reported by the author's group

must be trapped with an alcohol trap and an in-line aqueous $NaHCO_3$ trap.

Base-free in situ photo-on-demand synthesis of chloroformate and one-pot syntheses of carbonate esters and carbamates

Chloroformate plays important roles in organic synthesis and is generally prepared from $COCl_2$ and an alcohol (Fig. 5) [38]. In our pioneering study of in situ photo-on-demand phosgenation reactions, we reported that chloroformate was produced in high yield upon photoirradiation of a $CHCl_3$ solution containing an alcohol with O_2 bubbling [25, 26]. This approach provided one-pot syntheses of unsymmetric carbonates and carbamates via subsequent addition of alcohols or amines, respectively.

When $CHCl_3$ solutions containing 20 mmol of a primary alkyl alcohol ($n = 0$, 1, 2, 3, or 6) in the above photochemical reaction system were exposed to UV light at

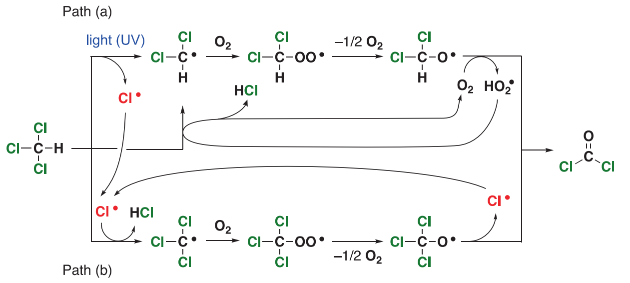
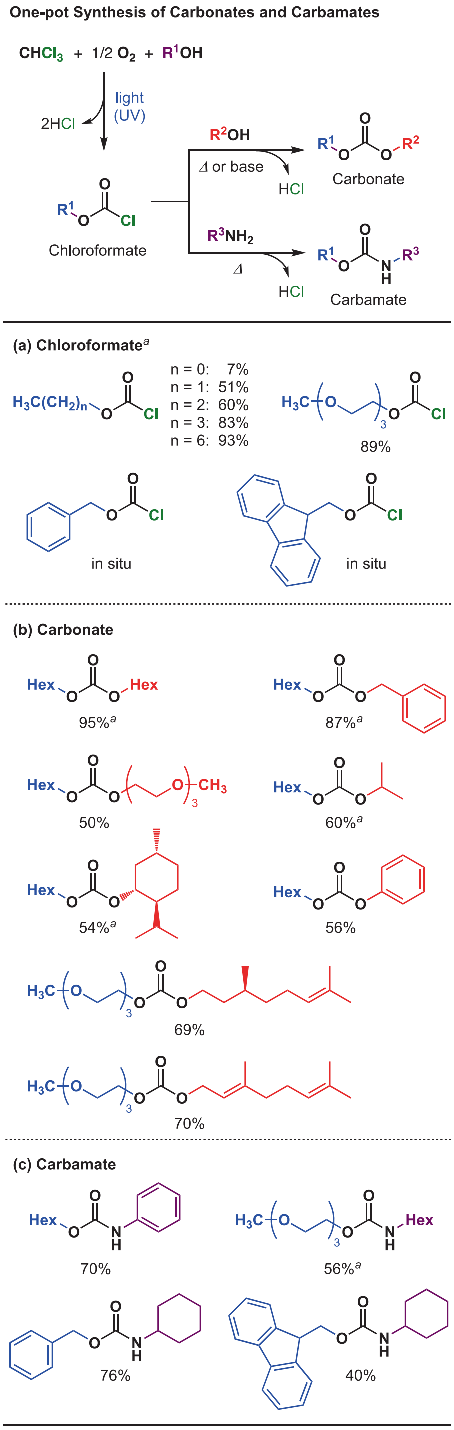


Fig. 4 Proposed mechanism for oxidative photochemical conversion of $CHCl_3$ to $COCl_2$

30 °C, the corresponding chloroformates were obtained as the major products in 7–93% yields. (Fig. 5a). Formates and carbonate esters were also obtained as minor products with ~5% yields. The chloroformate yield clearly decreased with decreasing alcohol chain length because the alkyl alcohols with shorter chain lengths evaporated more easily, which slowed the photochemical conversion of $CHCl_3$ to $COCl_2$ in the gas phase. In support of this proposed mechanism, the reaction was decelerated dramatically when the reaction temperature was raised to 50 °C, which may have vaporized both the alcohol and $COCl_2$ in the $CHCl_3$. Longer irradiation times also tended to decrease the product yields, most likely due to photodecomposition of the products. With the concentration of alcohol, the temperature, and the irradiation time optimized, triethylene glycol monomethyl ether (TEGM) was converted to the corresponding chloroformate in 89% yield. Although aryl alcohols, which are generally less nucleophilic than alkyl alcohols, showed no notable reaction, aryl-substituted aliphatic alcohols such as benzyl alcohol and 9-fluorenylmethanol provided the corresponding chloroformates.

This reaction enables the preparation of $CHCl_3$ solutions containing chloroformates, and thus, these solutions are available for one-pot syntheses of unsymmetric carbonate esters and carbamates (Figs. 5b and 5c). An as-prepared $CHCl_3$ solution of *n*-hexyl chloroformate was stirred at 30–70 °C for 1–3 h to remove the HCl, and the unreacted $COCl_2$ dissolved in the sample solution. Since the carbonyl carbon in chloroformate is less electrophilicity than that of $COCl_2$, the second substitution reaction with an alkyl alcohol to form the carbonate ester occurs slowly when the sample solution is heated. For example, when 1.5 equiv. of 1-hexanol was added into a $CHCl_3$ solution containing chloroformate, and the sample solution was stirred for 15 h at 90 °C to evaporate the $CHCl_3$ solvent from the system, the corresponding symmetric carbonate was obtained in 95% yield (isolated amount and yield: 1.29 g and 56%, respectively). With a similar procedure, benzyl alcohol and TEGM provided unsymmetrical carbonates in 87% and 50% yields, respectively. 2-Propanol, a secondary alcohol, did not react without a base, but the corresponding unsymmetrical carbonate was obtained in 60% yield upon addition of pyridine. (–)-Menthol, with a boiling point higher than that of 2-propanol, underwent the reaction without a base and at a higher temperature to give the corresponding carbonate in 54% yield. Although phenol, an



[a] Yield determined by ^1H NMR analysis.

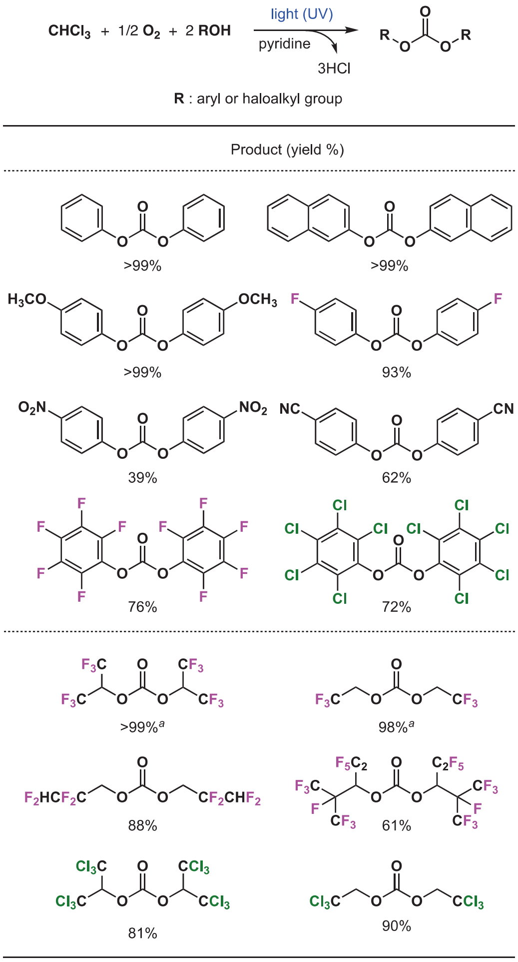
Fig. 5 In situ photo-on-demand synthesis of (a) chloroformates and one-pot syntheses of (b) symmetric and unsymmetric carbonates and (c) carbamates aryl alcohol which is less nucleophilic than alkyl alcohols, did not react with chloroformate even at elevated temperatures, it underwent the reaction after triethyl amine (TEA) was added and provided the asymmetric hexyl phenyl carbonate in 56% yield. With similar one-pot procedures, biobased nonionic amphiphiles were synthesized from $CHCl_3$ solutions of TEGM. The TEGM underwent an initial photochemical conversion in $CHCl_3$ to form the corresponding chloroformate, and subsequent addition of citronellol or geraniol to the sample solution and heating provided the corresponding amphiphilic carbonates in 69% and 70% yields, respectively.

The introduction of *N*-protecting groups to amines is an important application of chloroformates [39]. One-pot syntheses of carbamates were also achieved upon addition of an amine to the prepared $CHCl_3$ solution of chloroformate (Fig. 5c). For example, the photochemical conversion of 1-hexanol to the corresponding chloroformate in $CHCl_3$ and a subsequent reaction with aniline under reflux generated the carbamate in 70% yield based on the alcohol (isolated amount and yield: 1.13 g and 48%, respectively) with the elimination of HCl. With a similar procedure, an amphiphilic carbamate was also synthesized from TEGM in 56% yield. Cbz- and Fmoc-protection of cyclohexylamine were then achieved with this one-pot procedure.

Base-promoted in situ photo-on-demand syntheses of carbonate esters and polycarbonates

$COCl_2$ and chloroformates undergo faster condensation reactions with alcohols in the presence of a base, which serves as a catalyst as well as an HCl scavenger. Since organic bases such as TEA and pyridine absorb UV light [40, 41], difficulties were anticipated for in situ photo-on-demand syntheses of carbonate esters with $CHCl_3$ solutions containing a mixture of alcohol and organic base, both of which inhibit the photooxidation of $CHCl_3$. In fact, the amount of $COCl_2$ generated by photooxidation of $CHCl_3$ (30 mL, 0.37 mol) decreased to 46% when 0.03 mol (8%) of pyridine was added. However, the reactions occurred with aryl alcohols and haloalkyl alcohols to give the corresponding carbonate esters (Fig. 6). This reaction provides convenient in situ photo-on-demand syntheses of carbonate esters in high yields on a gram scale [28].

When the photoreactions were conducted by adding 3.5 equiv. of pyridine to $CHCl_3$ solutions containing ethanol (EtOH) or 2-propanol (2-PrOH), neither the carbonate ester nor the chloroformate was obtained (data not shown). Both pyridine and alcohol inhibit the oxidative photodecomposition of $CHCl_3$ by absorbing UV light and/or trapping the radical species generated from $CHCl_3$.



aYield determined by ¹H NMR analysis.

Fig. 6 In situ photo-on-demand syntheses of carbonate esters with $CHCl_3$ solutions containing alcohols and pyridine

Although phenol, whose nucleophilicity is lower than those of alkyl alcohols, also showed no reaction in the absence of a base, the phosgenation reaction occurred to give diphenyl carbonate (DPC) in >99% yield (isolated amount: 1.1 g) in the presence of 5 equiv. of pyridine. Phenol is relatively more acidic ($pK_a = 10.0$) than alkyl alcohols ($pK_a = 15–18$) [42], and pyridine forms a weak acid–base complex with phenol with an association constant of $K = 33\ M^{-1}$ in $CHCl_3$ solution at 20 °C. This interaction may decelerate radical trapping and accelerate the nucleophilic additions of phenol to $COCl_2$ and chloroformate. 2-Naphthol, which has a larger π-conjugated structure, and 4-methoxyphenol, which contains an electron-donating methoxy group, have lower and higher pK_a values, respectively, (9.51 and 10.05, respectively) than phenol and provided the corresponding carbonate esters in >99% yields [43, 44]. 4-Fluorophenol, with an electron-withdrawing F on the phenol ring, provided the corresponding carbonate esters in 93% yield. Furthermore, 4-nitrophenol and 4-cyanophenol contain electron-withdrawing substituents and were converted to the

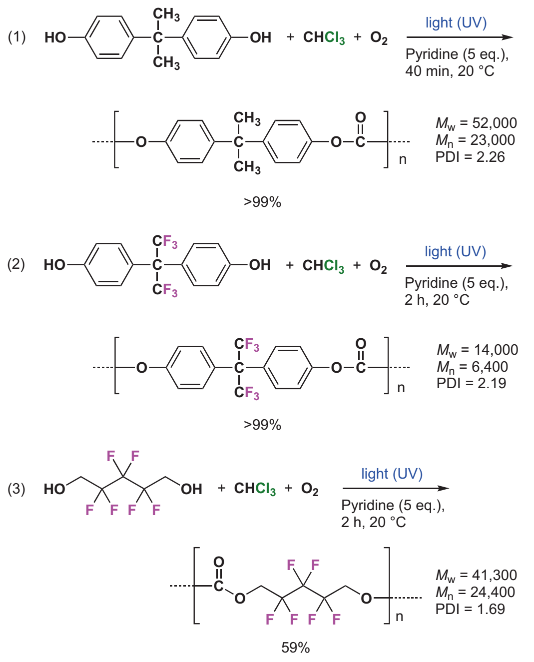


Fig. 7 In situ photo-on-demand syntheses of polycarbonates with $CHCl_3$ solutions containing diols and pyridine

corresponding carbonate esters in 39% and 62% yields, respectively. Even with pentachlorophenol and pentafluorophenol, which have lower pK_a values of 4.96 and 5.53 [45, 46], respectively, the reactions occurred with high yields.

Fluorinated alkyl alcohols, which are relatively acidic and form acid–base complexes, also participated in situ photochemical syntheses of carbonate esters in $CHCl_3$ solutions containing a mixture of the alcohol and a base. For example, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), which forms a pyridine complex with $K = 58\,M^{-1}$ in $CHCl_3$ at 20 °C, underwent a reaction in the presence of 2 equiv. of pyridine to produce the corresponding carbonate ester (BHFC) in quantitative yield. 2,2,2-Trifluoroethanol and 2,2,3,3-tetrafluoro-1-propanol, whose pK_a values are higher than that of HFIP, were also converted to the corresponding carbonate esters in 98 and 88% yields, respectively. A highly fluorinated alkyl carbonate was then synthesized from 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)pentan-3-ol in 61% yield. The reaction also occurred with chlorinated alkyl alcohols. HFIP and 2,2,2-trichloroethanol provided the corresponding carbonate esters in 81 and 90% yields, respectively.

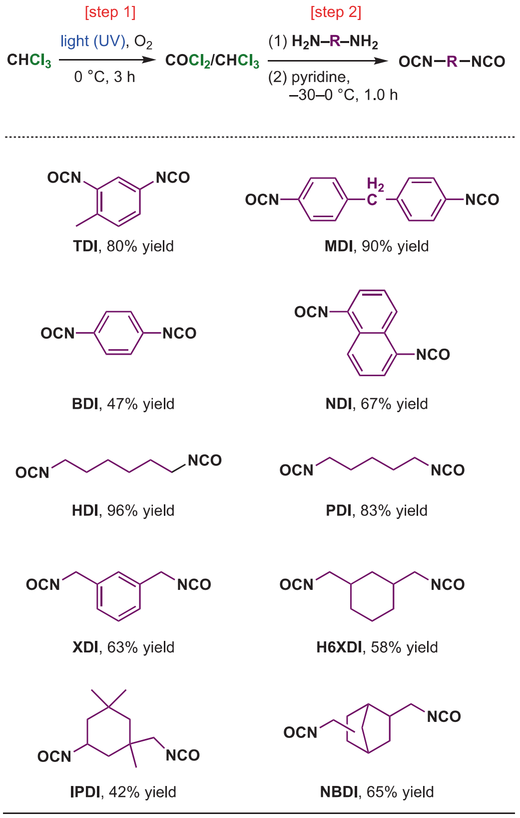
These base-promoted in situ photo-on-demand syntheses of carbonate esters were also available for the syntheses of PCs from diols (Fig. 7). Bisphenol A (BPA) provided a quantitative yield for a conventional PC (isolated amount: 2.7 g) with an average molecular weight of $M_w = 52{,}000$, $M_n = 23{,}000$, and PDI = 2.26. Bisphenol AF (BPAF), which contains electron-withdrawing trifluoromethyl groups, provided a PC with $M_w = 14{,}000$, $M_n = 6{,}400$, and PDI = 2.19. The lower molecular weight may be ascribed to the lower nucleophilicity of BPAF relative to that of BPA. 2,2,3,3,4,4-Hexafluoro-1,5-pentanediol, a fluoroalkyl diol, afforded the corresponding PC in 59% yield with $M_w = 41{,}300$, $M_n = 24{,}400$, and PDI = 1.69. The low solubility of the fluoroalkyl PC in organic solvents reduced the isolated yield.

In situ syntheses of isocyanates, blocked isocyanates, and polyurethanes with photo-oxidized $CHCl_3$

Isocyanates contain $-N=C=O$ groups and are typically synthesized industrially from amines and $COCl_2$ [4–10]. Alternatively, to avoid the direct use of $COCl_2$ in laboratory-scale experiments and small-scale industrial production, BTC is used in synthesizing isocyanates [2, 15]. We recently reported that the following two reactions involving in situ photochemical oxidation of $CHCl_3$ to $COCl_2$ allowed selective syntheses of *N*-substituted ureas and isocyanates from amines: [30] (I) UV photoirradiation of a $CHCl_3$ solution containing an amine and an organic base with O_2 bubbling at 20–40 °C provided the *N*-substituted urea. (II) A two-step reaction involving photochemical oxidation of $CHCl_3$ at low temperature and subsequent sequential injections of an amine and organic base into the sample solution provided the isocyanate. Processes (I) and (II) proceed with relative concentrations of $[COCl_2] < [amine]$ and $[COCl_2] > [amine]$, respectively, to provide the 1:2 and 1:1 reactions.

The amount of the $COCl_2$ generated in a 20 mL $CHCl_3$ solution was estimated to be 18.5 mmol after exposure to UV light from a 20 W LPML at 0 °C for 1 h while bubbling O_2 at a flow rate of 0.1 L/min. Based on this result, several diisocyanates that are conventionally used to manufacture PUs industrially were synthesized with $[COCl_2]>[amine]$ concentration ratios (Fig. 8). Toluene diisocyanate (TDI), methylenediphenyl diisocyanate (MDI), benzene diisocyanate (BDI), and naphthalene diisocyanate (NDI), which are aromatic diisocyanates, were synthesized in 80%, 90%, 47%, and 67% yields, respectively, from the corresponding diamines (5 mmol). Hexamethylene diisocyanate (HDI) and pentamethylene diisocyanate (PDI), which are alkyl diisocyanates, were synthesized in 96% and 83% yields, respectively. Cyclic diisocyanates, such as *m*-xylylene diisocyanate (XDI), 1,4-bis(isocyanatomethyl)cyclohexane (H6XDI), isophorone diisocyanate (IPDI), and norbornanediisocyanate (NBDI), were obtained in 63%, 58%, 42%, and 65% yields, respectively.

By preparing the diisocyanates in $CHCl_3$ solution, one-pot syntheses of biscarbamates, which serve as blocked



[a]Yield determined by ^1H NMR analysis.

Fig. 8 Two-step procedure used to synthesize diisocyanates with the in situ photo-on-demand synthesis of $COCl_2$ from $CHCl_3$ and subsequent addition of diamines[a]

isocyanates, were achieved (Fig. 9). When EtOH or HFIP was added to a $CHCl_3$ solution containing MDI, which was prepared with the two-step procedures described above without and with added pyridine, the corresponding biscarbamates were obtained in 78 and 71% yield, respectively. HDI, which is less reactive than MDI, also reacted with HFIP to give the corresponding biscarbamate with a lower yield of 37%. Fluorinated HDI (8FHDI), which is more reactive and unstable in air, was then prepared from a $CHCl_3$ solution containing the HCl salt of 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diamine (8FHDA·2HCl). The one-pot synthesis proceeded after addition of HFIP to the sample solution and afforded the corresponding biscarbamate in 37% yield.

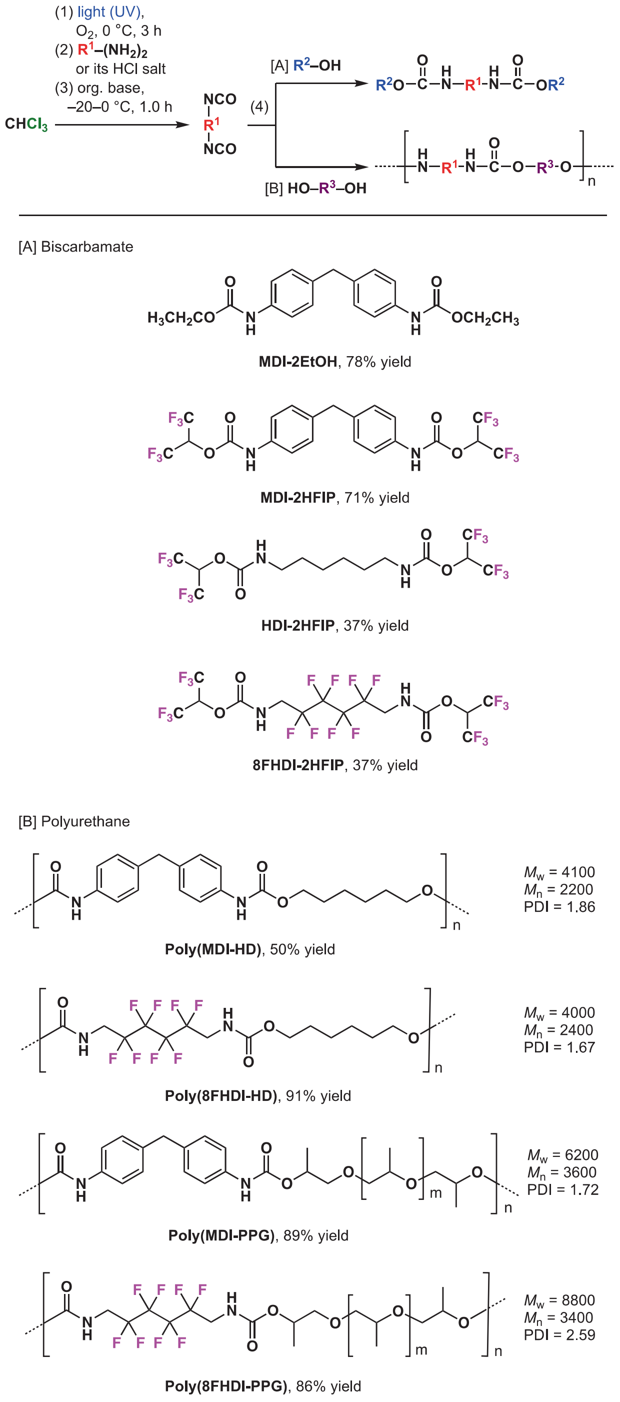


Fig. 9 One-pot syntheses of biscarbamates and polyurethanes from diamines through photochemical conversions to the corresponding diisocyanates

One-pot syntheses of polyurethanes (PU) were achieved by adding diols instead of monoalcohols to the diisocyanate $CHCl_3$ solutions. When an equimolar amounts of 1,6-hexanediol (HD) relative to the diamines were added to $CHCl_3$ solutions containing MDI or 8FHDI, the corresponding PUs [poly(MDI-HD) or poly(8FHDI-HD)] were obtained in 50% and 91% yields (isolated amounts: 0.92 and 0.81 g, respectively) with average molecular weights of $M_w = 4100$, $M_n = 2200$, PDI = 1.86 and $M_w = 4000$, $M_n = 2400$, PDI = 1.67, respectively. Their relatively low average molecular weights may have originated from the poor solubility of the formed PUs. Then, polypropylene glycol (PPG) with an average molecular weight of 400 increased the solubility of the PU and provided poly(MDI-PPG) and poly(8FHDI-PPG) in 89 and 86% yields (isolated amounts:

2.91 and 1.18 g, respectively) with $M_w = 6200$, $M_n = 3600$, PDI = 1.72, and $M_w = 8800$, $M_n = 3400$, PDI = 2.59, respectively. The average molecular weight of the PU formed in this one-pot synthesis can be controlled by estimating the amount of the diisocyanate formed in the sample solution via spectroscopic and/or HPLC analyses.

Cl_2-promoted photochemical oxidation of $CHCl_3$ with visible light and application to one-pot organic syntheses

Compared with the conventional phosgenation reactions run with CO/Cl_2 or triphosgene, the photo-on-demand phosgenation reactions described above for $CHCl_3$ are safe, convenient, and inexpensive, but the use of the LPML causes unfavorable side reactions arising from photodecomposition of both reagents and products by the high-energy UV-C light. The use of mercury lamps has recently been avoided due to their large environmental impacts and associated health hazards [47]. This background motivated us to develop a novel photo-on-demand photocatalytic reaction using lower-energy visible light, which enables the use of light-emitting diodes (LEDs) and sunlight as light sources instead of LPMLs. We found that bubbling O_2 through a $CHCl_3$ solution containing ~2% Cl_2 caused photooxidation with the white LED light [31]. For example, when 30 mL of $CHCl_3$ subjected to O_2/Cl_2 bubbling was exposed to white light from a 9 W LED at 20 °C for 1.5 h, a 12.5% conversion to $COCl_2$ resulted. The added Cl_2 may have served as a visible light-responsive initiator for the radical chain reaction of $CHCl_3$ and O_2 (Fig. 4) [48].

This photochemical reaction using visible light provided one-pot syntheses of chloroformates, carbonate esters, and isocyanates (Fig. 10). However, it is important to note that the reaction should be performed with a two-step procedure since some of the alkyl alcohols and amines used as reactants react with Cl_2. Using this method, hexyl chloroformate was synthesized quantitatively from a $CHCl_3$ solution (50 mL) containing 1-hexanol (30 mmol) without the need for an organic base. Dibutyl carbonate (DBC), DPC, and BHFC were also synthesized in 95, 84, and 70% yields via base-catalyzed condensation reactions. Furthermore, 1-isocyanatohexane, isocyanatobenzene, and (3-isocyanatopropyl)trimethoxysilane were synthesized in >99, 73, and 56% yields, respectively.

Conclusion

We have focused this review on our recent studies of in situ photo-on-demand phosgenation reactions of alcohols and amines, which were used to synthesize PCs, PUs, and their precursors such as chloroformates, carbonate esters, and diisocyanates in batch reactions. Given the current global warming problem, sustainable synthetic methods for polymer production are being actively studied. This photochemical reaction efficiently converts $CHCl_3$ to $COCl_2$, which is extremely reactive toward nucleophiles, and this enables in situ syntheses of many organic chemicals and polymers while reducing energy consumption and waste generation. We believe that the present in situ photo-on-demand phosgenation reaction has advantages over conventional phosgenation reactions, especially in terms of safety and environmental impact. When combined with the flow photo-on-demand phosgenation system reported recently by our group [34], which enables scale-up of chemical processes, our present findings are expected to provide practical polymer syntheses of use in both academia and industry. Our group is currently developing suitable facilities for the safe use of this photo-on-demand phosgenation reaction on a larger scale and is constructing a reaction library describing the syntheses of various organic chemicals, including polymers, for eventual commercial use.

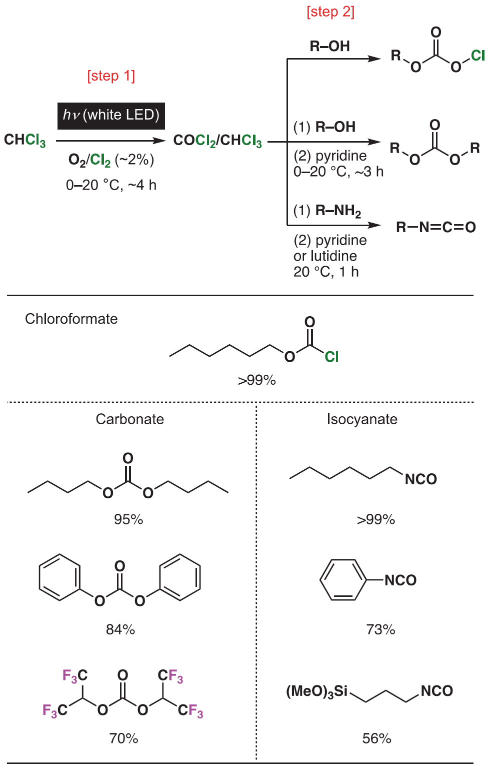


Fig. 10 Stepwise one-pot photochemical syntheses of chloroformates, carbonate esters and isocyanates from $CHCl_3$ and alcohols or primary amines with a 9 W white LED

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Compliance with ethical standards

Conflict of interest The author declares no competing interests.

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