ORGANIC LETTERS

2012
Vol. 14, No. 13
3376–3379

Photochemical Molecular Storage of Cl_2, HCl, and $COCl_2$: Synthesis of Organochlorine Compounds, Salts, Ureas, and Polycarbonate with Photodecomposed Chloroform

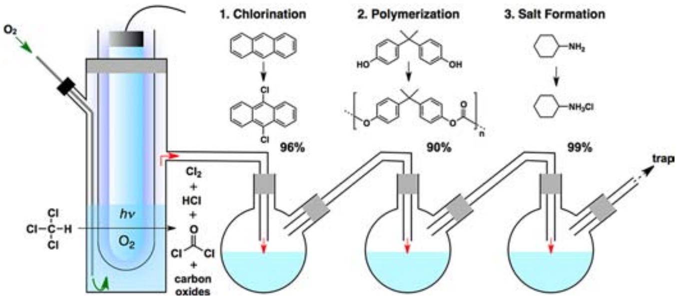
Yuki Kuwahara, Ailing Zhang, Haruka Soma, and Akihiko Tsuda*

Department of Chemistry, Graduate School of Science, Kobe University,
1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan

tsuda@harbor.kobe-u.ac.jp

Received May 16, 2012

ABSTRACT



Chloroform is available as not only an organic solvent but also photochemical molecular storage for synthetically important chemicals such as Cl_2, HCl, and $COCl_2$. We have succeeded in synthesizing organochlorine compounds, hydrochloric salt of amines, ureas, organic carbonates, and polycarbonate in practical high yields with photodecomposed chloroform.

Liquid chlorinated methanes, with high chemical stability, volatility, and ability to dissolve a wide range of organic compounds, are useful solvents for many chemical processes in the research laboratory and in industrial settings. On the other hand, their degradations via chemical or physical procedures have been also actively studied in the fields of green chemistry and environmental science.[1−7] For example, chloroform undergoes oxidative photodecomposition to give Cl_2, HCl, and carbon oxides such as CO, CO_2, and $COCl_2$ (phosgene) through a possible reaction mechanism as represented in Scheme 1.[6] These compounds, except for CO_2, are extremely toxic but are also very important reagents in a variety of chemical reactions. The phenomenon has never been seen in organic synthesis before, and we found herein that chloroform works as a photochemical molecular storage for those chemicals in the reactions. To avoid experimental hazards, chemists can temporarily convert highly toxic/caustic reagents into different compounds with no or low toxicity/causticity, for easy handling in liquid or solid states, and then utilize them in the target reactions via their chemical

---

(1) Kent, C. *Basics of Toxicology*; John Wiley & Sons Inc: New York, 1998.

(2) (a) Clove, A. M. *J. Am. Chem. Soc.* **1923**, *45*, 3133–3138. (b) Chapman, A. T. *J. Am. Chem. Soc.* **1935**, *57*, 419–422.

(3) Davis, D. D.; Schmidt, J. F.; Neeley, C. M.; Hanrahan, R. J. *J. Phys. Chem.* **1975**, *79*, 7–11.

(4) Vogel, M. T.; Criddle, S. C.; McCary, L. P. *Environ. Sci. Technol.* **1987**, *21*, 722–736 (Review).

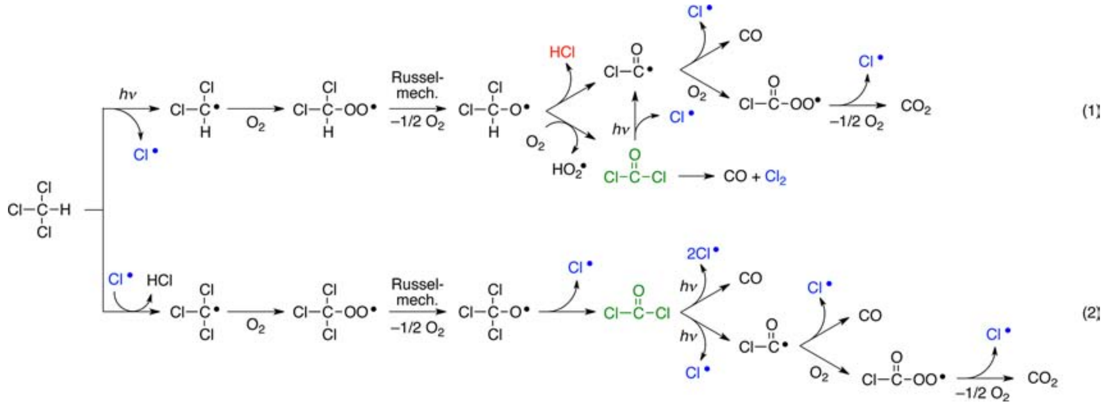
(5) (a) Kondo, M. M.; Jardim, W. F. *Water Res.* **1991**, *25*, 823–827. (b) Halmann, M.; Hunt, A. J.; Spath, D. *Sol. Energy Mater. Sol. Cells* **1992**, *26*, 1–16. (c) Wong, J. C. S.; Linsebigler, A.; Lu, G.; Fan, J.; Yates, J. T., Jr. *J. Phys. Chem.* **1995**, *99*, 335–344. (d) Chen, M.-T.; Lien, C.-F.; Liao, L.-F.; Lin, J.-L. *J. Phys. Chem. B* **2003**, *107*, 3837–3843.

(6) Alapi, T.; Dombi, A. *Chemosphere* **2007**, *67*, 693–701.

(7) (a) Sanhueza, E.; Hisatsuna, I. C.; Heicklen, J. *Chem. Rev.* **1976**, *76*, 801–826. (b) Pruden, L. A.; Ollis, F. D. *J. Catal.* **1983**, *82*, 404–417. (c) Gürtler, R.; Möller, U.; Sommer, S.; Müller, H.; Kleinermanns, K. *Chemosphere* **1994**, *29*, 1671–1682. (d) Shirayama, H.; Tohezo, Y.; Taguchi, S. *Water Res.* **2001**, *35*, 1941–1950. (e) Prager, L.; Hartmann, E. *J. Photochem. Photobiol. A: Chem.* **2001**, *138*, 177–183. (f) Zuo, G.-M.; Cheng, Z.-X.; Chen, H.; Li, G.-W.; Miao, T. *J. Hazard. Mater.* **2006**, *128*, 158–163.

10.1021/ol301356r

Scheme 1. Possible Reaction Pathways for Oxidative Photodecomposition of Chloroform



regenerations in situ. For example, $COCl_2$, which is an extremely toxic gas at rt but a very important C1 building block for the industrial synthesis of a variety of compounds, is frequently used in situ by generation through the decomposition of triphosgene with a base.[8] Here, the triphosgene molecule works as chemical storage for $COCl_2$. Thus, the photochemical multigeneration of synthetically useful Cl_2, HCl, and $COCl_2$ from chloroform furnishes greater chemical benefits as well as scientific advancements into a variety of organic syntheses and material sciences especially in laboratory scale experiments. Since chloroform is a commonly used solvent in organic synthesis, it also has an advantage of being low cost molecular storage for those chemicals.

Kawai reported in 1966 a pioneer example, where 1,3-diphenylurea was isolated on an analytical scale by the addition of aniline into a photodecomposed chloroform solution, prepared upon exposure to light with a fluorescent lamp under air, with the purpose of identifying the phosgene generated in the solution.[9] However, we recently reported that liquid brominated methanes are photoresponsive molecular storage for elemental Br_2, where they efficiently generate elemental Br_2 upon oxidative photodecomposition.[10] By taking advantage of in situ generation of Br_2 from the organic solvent itself, many organobromine compounds could actually be synthesized easily as well as safely in practical high yields. With this background, we found herein that chloroform upon exposure to UV light under O_2 generates multichemical reagents such as Cl_2, HCl, and $COCl_2$, which are actually available for a wide variety of syntheses such as organochlorine compounds, hydrochloric salts, ureas, organic carbonates, and polycarbonate in practical high yields (Table 1).

The low-pressure mercury lamps, most of which have low electric power consumption, mainly generate ultraviolet light with wavelengths of 184.9 and 253.7 nm, which cover electronic absorption bands of chlorinated methanes due to $\sigma-\sigma^*$ and/or $n-\sigma^*$ transitions.[11] The lamp (20 W, ~24 mm × 120 mm) was inserted into the solution via a quartz glass jacket (~28 mm) fixed in the center of a cylindrical flask (~42 mm) (Figure 1A), where the photoirradiation of pure chloroform (40 mL) at 20 °C under O_2 actually generated small gas bubbles due to its photodecomposition (Supporting Information movie). With this photoreaction system under a steady flow of O_2 (50 mL/min) bubbled through the chloroform, a 12% decrease in weight, including an ~3% volatilization loss was evaluated experimentally,[12] after the photoreactions for 1 h. The reactions may proceed as a possible mechanism of initial

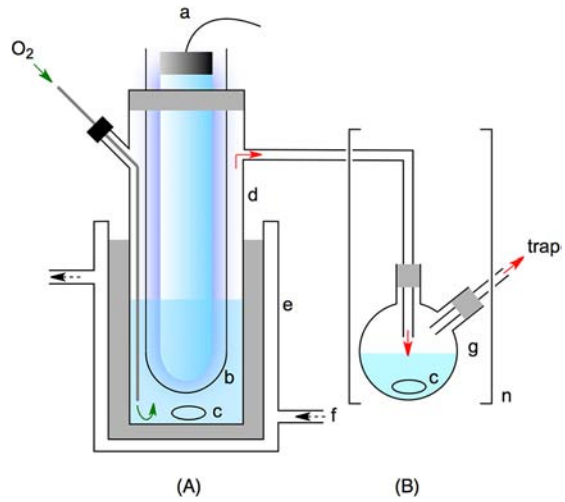


Figure 1. Schematic illustration of an experimental setup for photodecomposition of chloroform (A) and for reactions of substrates with the photodecomposed chloroform (B) under flowing O_2. (a) Low-pressure mercury lamp (20 W, ~24 × 120 mm); (b) quartz glass jacket (~30 mm); (c) stirring bar; (d) cylindrical flask (~42 mm); (e) water bath; (f) cooling medium; (g) two-neck round-bottom flask (n = 1 or 3).

---

(8) Kavala, V.; Naik, S.; Patel, B. K. *J. Org. Chem.* **2005**, *70*, 4267–4271.

(9) Kawai, S. *Yakugaku Zasshi* **1966**, *86*, 1125–1132.

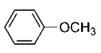
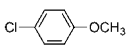
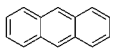
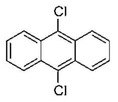
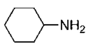
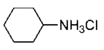
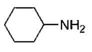
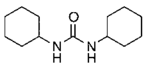
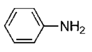
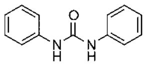
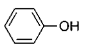
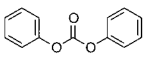
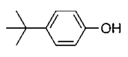
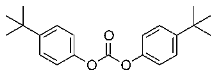
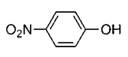
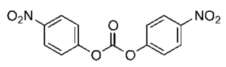
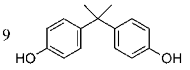
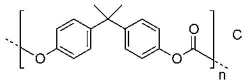
(10) Kawakami, K.; Tsuda, A. *Chem.—Asian, J.*, in press (asia.201200322).

photolytic cleavage of a C−Cl bond, and subsequent reactions of the resulting halomethane radicals with O_2 finally generate carbon oxides with eliminations of Cl_2 and HCl via formation of $COCl_2$ (Scheme 1).[6,13] Since $COCl_2$ is soluble in organic solvents, ^{13}C NMR spectroscopy of a $CDCl_3$ solution, which had been exposed to the gas including photodecomposed products of chloroform for 1.0 h at 0 °C, actually showed only a strong singlet signal at δ = 143.22 ppm, originating from $COCl_2$ (Figure S1). On the other hand, the resulting photodecomposed $CHCl_3$ solution after exposure to UV light contained not only the above volatile products but also C−C coupled products. Solid C_2Cl_6 could actually be isolated in 0.1% yield from the remaining chloroform solution after exposure to light for 1.0 h and subsequent washing of the solution with water. C_2Cl_6 may form through a radical coupling reaction of trichloromethyl radicals, generated in the course of photodecomposition reactions (Scheme 1). The observed photodecomposition of chloroform also occurred under flowing natural air, containing moisture, or in the presence of a little amount of ethanol, which has been used as a stabilizer in commercially available chloroform.[9]

With the above experimental results for photodecomposition of chloroform in mind, we then demonstrated some possible organic reactions for the reactive photodecomposed products of Cl_2, HCl, and $COCl_2$ with appropriate reaction substrates. These photodecomposed products, especially $COCl_2$, are extremely toxic, but following procedures developed in this study will allow their application into a variety of reactions without hazardous handling, expensive experimental settings, or otherwise harsh conditions. As illustrated in Figure 1, the reactions can be demonstrated in a pseudoclosed system, where the reaction substrate dissolved in organic solvents is exposed to the photodecomposed chloroform gas, prepared by photoirradiation under flowing O_2. The unreacted photodecomposed products, after passing through the reaction system, must be trapped and neutralized by water containing $NaHCO_3$ at the terminal of the reaction system. With this system, when 8.3 mmol of anisole, dissolved in 15 mL of chloroform, was exposed for 1 h to the photodecomposed chloroform/O_2 gas at rt, 4-chloroanisole was obtained in 90% isolated yield (Table 1, entry 1). Anthracene also underwent chlorination to give 9,10-dichloroanthracene in 97% yield (entry 2). Here, Cl_2 included in the photodecomposed products may allow the observed chlorination reaction.[14] On the other hand, amines dissolved in methanol, whose solvent allows dissolution of polar species and decomposition of $COCl_2$,[15] provided their HCl salts quantitatively upon exposure to the gas. For example, a methanol solution of cyclohexylamine provided its HCl salt in 99% yield after the reaction for 1 h (entry 3). However, interestingly, cyclohexylamine dissolved in chloroform upon exposure to the gas gave not only the HCl salt but also 1,3-dicyclohexylurea in 19% isolated yield, which most likely formed through the reaction of the amine with $COCl_2$ (entry 4-I).[16] In order to trap HCl, which may prevent substitution reactions of the amine to $COCl_2$, 5 equiv amounts of triethylamine (TEA) were added into the solution, and then, the yield was dramatically increased to 99% yield (entry 4-II). Aniline also converted to the corresponding ureas in the solution containing 5 equiv of TEA in 76% yield (entry 5). These reactions described above also occurred under flowing natural air instead of O_2 gas in analogous high yields, but no reactions were observed without photoirradiation.

Table 1. Syntheses of Organochlorine Compounds, HCl Salt of Amine, Ureas, and Carbonates with Photodecomposed Chloroform[a]

$$\text{substrate} \xrightarrow[\text{solvent}]{\text{photodecomposed CHCl}_3\ \text{(gas)}} \text{product}$$

entry	substrates	products	solvent	Et_3N (equiv)	yield (%)[b]
1			$CHCl_3$	–	90
2			$CHCl_3$	–	94
3			CH_3OH	–	>99
4			(I) $CHCl_3$	–	19
			(II) $CHCl_3$	5.0	>99
5			$CHCl_3$	5.0	76
6			(I) $CHCl_3$	–	trace
			(II) $CHCl_3$	3.5	>99
7			$CHCl_3$	3.5	>99
8			$CHCl_3$	3.5	>99
9			$CHCl_3$	7.0	90

[a] Reactions were carried out with 0.6−8.3 mmol of substrates in 15 mL of organic solvent upon exposure to the photodecomposed chloroform gas for 0.5−1.0 h at rt. [b] Isolated yields are given.

---

(11) Russel, R. B.; Edwards, O. L.; Raymonda, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 2129–2133.

(12) The volatilization loss was evaluated from the decrease in weight of 40 mL of chloroform in the cylindrical flask by bubbling with O_2 (50 mL/min) for 1 h, where the lamp, wrapped with aluminum foil, illuminated in the quartz glass jacket fixed in the flask.

(13) McGivern, W. S.; Kim, H.; Francisco, J. S.; North, S. W. *J. Phys. Chem. A* **2004**, *108*, 7247–7252.

(14) Watson, W. D. *J. Org. Chem.* **1982**, *47*, 5270–5276.

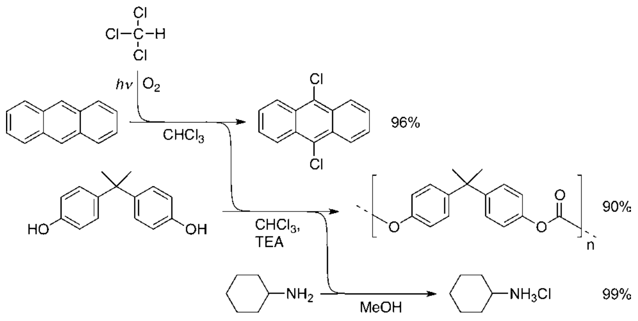
(15) Phosgene is known to give chloroformic esters through reactions with alcohols: Saunders, J. H.; Slocombe, R. J.; Hardy, E. E. *J. Am. Chem. Soc.* **1951**, *73*, 3796–3797.

(16) (a) Turner, W. R.; Werbel, L. M. *J. Med. Chem.* **1985**, *28*, 1728–1740. (b) Izdebski, J.; Pawlak, D. *Synthesis* **1989**, 423–425.

Next, we carried out the synthesis of organic carbonates with the photodecomposed chloroform. The organic carbonates can be synthesized in general through the reactions of phosgene and phenol derivatives with the assistance of a base catalyst, which can deprotonate the phenolic OH group.[17] By reference to the above procedures for the synthesis of urea derivatives, phenol, dissolved in chloroform containing 3.5 equiv of TEA, was exposed to the photodecomposed chloroform/O_2 gas. Then, the corresponding diphenylcarbonate was obtained in 99% yield after a reaction time of 1.0 h at rt (entry 6-II). As expected, the reaction hardly proceeded in the absence of TEA, which may work as both the base catalyst and the HCl trapping reagent (entry 6-I). 4-*tert*-Butylphenol and 4-nitrolphenol, having an electron-donating and -withdrawing group, respectively, also converted efficiently to the corresponding diarylcarbonates in 99% yields (entries 7 and 8, respectively). With this new synthetic methodology, efficient formations of carbonates without notable side products are observed, and we can further demonstrate the synthesis of polycarbonate through the reaction of 4,4′-isopropylidenediphenol (bisphenol A), having two hydroxy groups, and the photodecomposed chloroform.[18] When 15 mL of chloroform solution containing bisphenol A (456 mg, 2.0 mmol) and 7 equiv of TEA were exposed for 0.5 h to the photodecomposed chloroform/O_2 gas, the polycarbonate was obtained as a white powdery solid in 90% yield with an average molecular weight (M_w) of 43 000 having a polydispersity index of $M_w/M_n = 2.8$, determined by HPLC (entry 9, Figure S2).

Finally, to increase the atom economy of the reaction using the photodecomposed products of chloroform, we have demonstrated a triple synthesis of 9,10-dichloroanthracene, polycarbonate, and the HCl salt of cyclohexylamine with a sequential reaction system as schematically illustrated in Figure 1 ($n = 3$). This multireaction system exploits the advantage of heterogeneous gas–liquid reactions, which allow photodecomposed chloroform gas to pass through all reaction vessels with dominant consumptions of the necessary reagents in the order shown from the photoreactor. Considering the reaction features described above, the gas was first passed through a chloroform solution of anthracene, then a chloroform solution containing a 1:7 mixture of bisphenol A and TEA, and finally a methanol solution of cyclohexylamine (Scheme 2). After a reaction time of 1 h, we successfully obtained 9,10-dichloroanthracene, polycarbonate, and cyclohexylamine HCl salt in 96%, 90%, and 99% yield, respectively. Here, total elemental consumptions of carbon and chlorine atoms of the photodecomposed chloroform to these reactions could be evaluated approximately as 4% and more than 7%, respectively. These values will increase with future improvements of the reaction conditions and systems.

Scheme 2. Sequential Triple Reactions with Photodecomposed Chloroform



In conclusion, we found in this study that chloroform is not only an organic solvent but also photochemical molecular storage for synthetically important chemicals such as Cl_2, HCl, and $COCl_2$. High yield syntheses of organochlorine compounds, the hydrochloric salt of amines, ureas, organic carbonates, and polycarbonate were actually achieved through the reactions of substrates with the photodecomposed chloroform. This new synthetic methodology developed herein is widely applicable in all fields of chemistry. Its extension to other halomethanes, composed of hetero/homo combinations of H, F, Cl, Br, and I, is a fascinating project, which is now in progress in our laboratory.

Acknowledgment. The present work was sponsored by a Grant-in-Aid for Scientific Research (B) (No. 22350061) from the Ministry of Education, Science, Sports, and Culture, Japan, TEPCO Research Foundation, and a Toray Science and Technology Grant.

Supporting Information Available. Video for photodecomposition of chloroform, experimental details, ^1H and ^{13}C NMR spectra of the products, and SEC profile and photograph of the polycarbonate obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

---

[17] (a) Van, H. H. H. M.; Maas, C. J. J.; Vander Wekke, L.; Oyevaar, M. H. Eur. Pat. Appl., 596206, 1994. (b) Matsumoto, K.; Kyoshige, K. *Jpn. Kokai Tokkyo Koho* **1994**, 06293708. (c) Hara, Y.; Koto, H.; Higashijima, M. *Jpn. Kokai Tokkyo Koho* **1997**, 09024278.

[18] (a) Brunelle, D. J.; Boden, E. P.; Shannon, T. G. *J. Am. Chem. Soc.* **1990**, *112*, 2399–2402. (b) Serini, V. *Polycarbonates, Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2000.