Brominated Methanes as Photoresponsive Molecular Storage of Elemental Br$_2$

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FULL PAPER

Abstract: The photochemical generation of elemental Br_2 from brominated methanes is reported. Br_2 was generated by the vaporization of carbon oxides and HBr through oxidative photodecomposition of brominated methanes under a 20 W low-pressure mercury lamp, wherein the amount and situations of Br_2 generation were photochemically controllable. Liquid CH_2Br_2 can be used not only as an organic solvent but also for the photoresponsive molecular storage of Br_2, which is of great technical benefit in a variety of organic syntheses and in materials science. By taking advantage of the in situ generation of Br_2 from the organic solvent itself, many organobromine compounds were synthesized in high practical yields with or without the addition of a catalyst. Herein, Br_2 that was generated by the photodecomposition of CH_2Br_2 retained its reactivity in solution to undergo essentially the same reactions as those that were carried out with solutions of Br_2 dissolved in CH_2Br_2 that were prepared without photoirradiation. 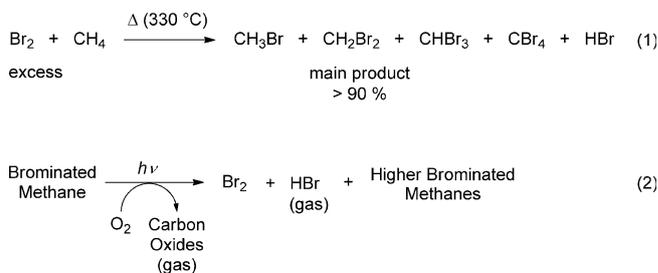Furthermore, HBr, which was generated during the course of the photodecomposition of CH_2Br_2, was also available for the substitution of the OH group for the Br group and for the preparation of the HBr salts of amines. Furthermore, the photochemical generation of Br_2 from CH_2Br_2 was available for the area-selective photochemical bleaching of natural colored plants, such as red rose petals, wherein Br_2 that was generated photochemically from CH_2Br_2 was painted onto the petal to cause radical oxidations of the chromophoric anthocyanin molecules.

Keywords: bleaching · bromine · molecular storage · photochemistry · vaporization

Introduction

Elemental Br_2 is one of the most-useful reagents for the syntheses of organobromine compounds and is used in a wide variety of organic reactions;[1] however, it is extremely corrosive, as well as toxic to living organisms. Br_2 is a fuming red/brown liquid at room temperature and it slowly vaporizes at room temperature, even when it is stored in screw-type vials through the interface of the glass wall and plastic cap. Thus, it is usually stored in glass ampules and corrosive-resistant steel tanks in the laboratory and in industrial settings, respectively. To avoid experimental hazards, chemists can temporarily convert toxic/caustic reagents into different compounds with non- or low toxicity/causticity or into easy-to-handle liquids or solids and utilize them in the target reactions through their in situ chemical regeneration. For example, phosgene, which has the chemical formula $COCl_2$ and is an extremely toxic gas at room temperature but is a very important building block for the industrial synthesis of a variety of compounds, is frequently used by its in situ generation through the decomposition of triphosgene with a base.[2] Effectively, triphosgene performs the molecular storage of phosgene. In the same way, the chemical storage of Br_2, instead of the conventional physical procedures, also furnishes great technical benefits, as well as scientific advancements, for a variety of organic syntheses and in material sciences.[3] Some inorganic salts that contain bromine, such as KBr, have been known to generate Br_2 through reactions with oxidizing reagents in acidic water and the resulting bromine water can bring about bromination reactions.[4] Whilst, *N*-bromosuccinimide (NBS) can also generate elemental Br_2 in CCl_4 upon heating, photoirradiation, or by reaction with a base, it is actually used as the bromine source in free-radical bromination reactions.[5,6] However, the generation of elemental Br_2 from these reagents occurs under specific conditions with the chemical contamination of the system by the resulting side-products and/or the added reagents. Against this background, herein, we report the photochemical generation of Br_2 from brominated methanes with the vaporization of the side-products, such as carbon oxides and HBr, upon exposure to UV light under O_2 (Scheme 1, Equation (2)). The resulting sample solutions

$$Br_2 + CH_4 \xrightarrow{\Delta\ (330\ °C)} CH_3Br + CH_2Br_2 + CHBr_3 + CBr_4 + HBr \quad (1)$$

excess $\qquad\qquad\qquad$ main product > 90 %

$$\text{Brominated Methane} \xrightarrow[\substack{O_2 \quad \text{Carbon} \\ \text{Oxides} \\ \text{(gas)}}]{h\nu} Br_2 + \underset{\text{(gas)}}{HBr} + \text{Higher Brominated Methanes} \quad (2)$$

Scheme 1. Thermochemical storage (1) and photochemical release (2) of Br_2 by using brominated methanes.

that contained elemental Br_2 are useful for a variety of applications, such as the synthesis of organobromine compounds in high practical yields and the macroscopic photochemical bleaching of colored plants that contain natural dye compounds. Because brominated methanes can be prepared from the thermal bromination reactions of CH_4 with Br_2, wherein Uner and co-workers have achieved above 90 % conversion of CH_4 with high CH_2Br_2 selectivity (above 90 %; Scheme 1, Equation (1)),[7] the reactions presented herein have accomplished the complete chemical storage and release of elemental Br_2 by using brominated methanes.

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The photodecomposition of chlorinated methanes has been actively studied in environmental science and sustainable chemistry because of their potential hazard to life and health and their properties as environmental pollutants.[8–14] For example, the photodecomposition of $CHCl_3$ proceeds through the generation of highly toxic $COCl_2$, CO, Cl_2, and HCl, together with CO_2 under an O_2 atmosphere. Some examples related to the photodecomposition of brominated methanes have also been reported at the analytical level. Lin and co-workers succeeded in detecting the molecular elimination of Br_2 in 248 nm photolysis of bromoform ($CHBr_3$) by using cavity ring-down absorption spectroscopy.[15c] North and co-workers reported a computational study of the atmospheric oxidation of CH_2Br_2 and $CHBr_3$ that was initiated by UV photolysis,[16] but no example has been reported for the experimental photodecomposition of the less-brominated CH_2Br_2. Because the photodecomposition of brominated methanes is still an ambiguous qualitative issue,[15–19] the use of their photodecomposed products has hardly attracted any attention as practically available elemental sources in organic synthesis and material sciences. Herein, we report that brominated methanes, in particular CH_2Br_2, upon exposure to UV light efficiently generate elemental Br_2, which is practically available for a variety of applications.

Abstract in Japanese:

液体のブロモメタン類に紫外線を照射すると、臭素が効率的に発生することを見出した。20 W 低圧水銀ランプを用いて、ブロモメタン類を酸素雰囲気下で光分解すると、気体のHBr や炭素酸化物の生成を伴って臭素を発生させることができ、その発生を任意に光化学的に制御できることを見出した。このようなジブロモメタンの性質は、それらを単なる有機溶媒でなく、光応答性の臭素貯蔵分子として利用することができることを示しており、有機合成やマテリアル科学などの様々な応用において大いに役立つことが期待される。本研究では実際に、液体のブロモメタン類から直接in situ でBr2 を発生させることができる利点を活かして、様々な有機臭素化合物を、簡便かつ高収率で得ることに成功した。ブロモメタン類の光分解により発生したBr2 は、その溶液中で通常の臭素と同等の反応性を有しており、また同時に発生したHBr を反応に利用することもできる。反応系中に触媒を加えることも可能であり、様々な臭素化反応を効率的に進行させることができる。加えて我々は、ジブロモメタンからの光臭素発生を利用して、バラの花びらなどの有色植物のエリア選択的光漂白に成功した。

Results and Discussion

Photochemical Generation of Br$_2$ from Brominated Methanes

Low-pressure mercury lamps, most of which have low electrical power consumption, typically generate ultraviolet light with wavelengths of 184.9 and 253.7 nm, which cover the electronic absorption bands of brominated methanes that are due to σ−σ* and/or n−σ* transitions (see the Supporting Information, Figure S1).[15,20] Thus, the lamp (20 W, 24× 120 mm) was inserted into the solution in a 28 mm quartz-glass jacket that was fixed in the center of a cylindrical flask (42 mm; Figure 1a). For example, in this glass vessel, the exposure of liquid CH_2Br_2 (10 mL) to UV light under a flow of O_2 (30 mL min^{-1}) at 40°C caused a gradual color change from colorless to brownish orange. Moreover a 4.6% de-
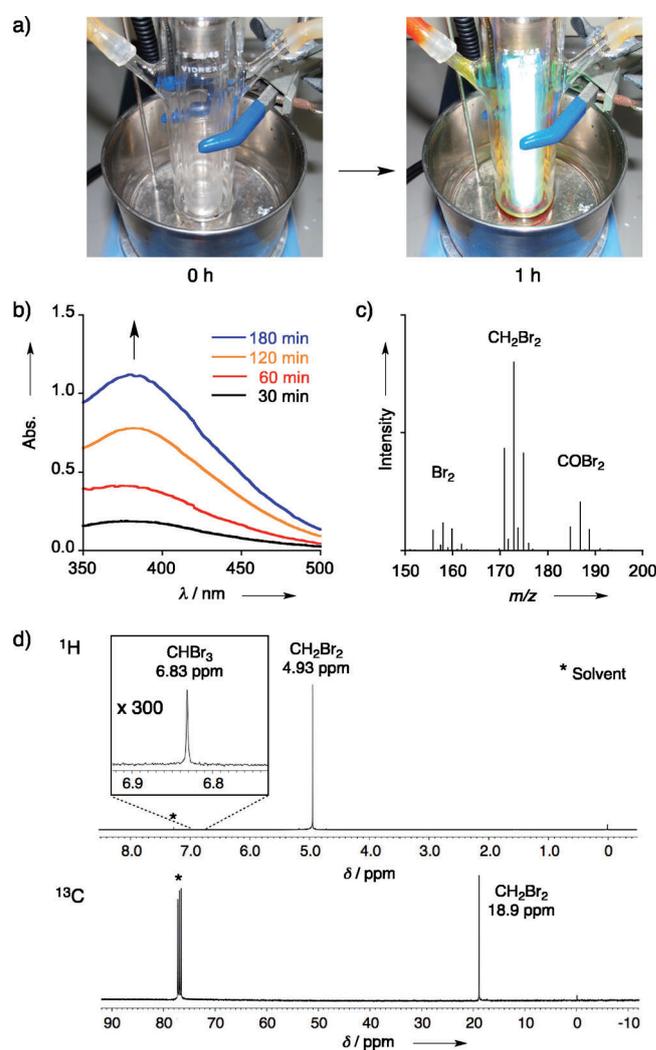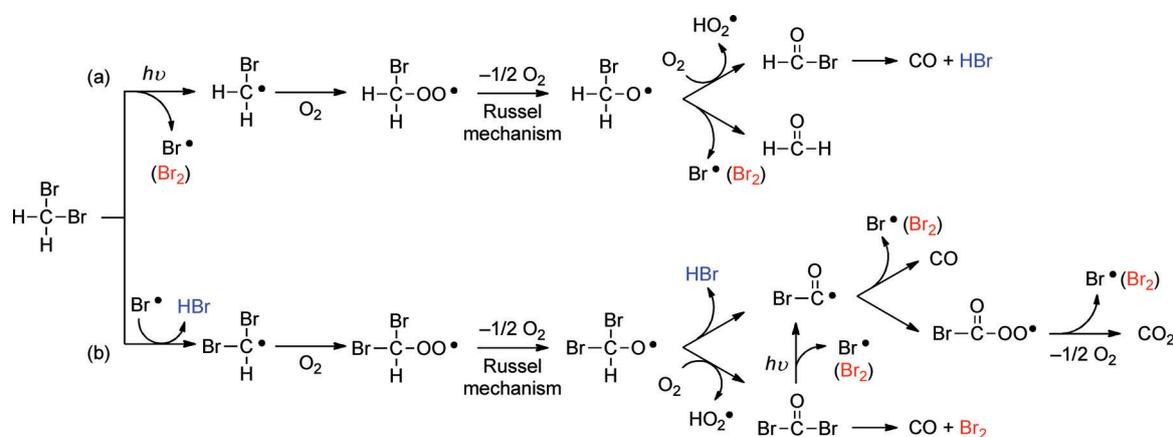

Figure 1. Photodecomposition of CH_2Br_2 upon exposure to UV light under a flow of O_2 at 40°C with a 20 W low-pressure mercury lamp. a) Photographs before and after photoirradiation. b) Changes in the absorption spectra of CH_2Br_2, measured upon 150-fold dilution with MeOH. c) GCMS and d) ^{1}H and ^{13}C NMR spectroscopy (CDCl$_3$) of photodecomposed CH_2Br_2 after photoirradiation for 3 h.

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crease in weight and approximately 0.8% volatilization versus the reference experiment without photoirradiation were observed after 3 hours, most likely owing to the generation of volatile photodecomposed products from CH_2Br_2. The absorption spectra of the sample solution, upon dilution with MeOH, showed a characteristic absorption band that corresponded to Br_2 in the UV/Vis region ($\lambda_{max} = 379$ nm, Figure 1b).[21] GCMS, which was used to qualitatively evaluate the photodecomposed products of CH_2Br_2, also indicated the presence of Br_2 and $COBr_2$ at $m/z = 160$ and 188, respectively, with their characteristic isotope patterns (Figure 1c).[16] However, no notable peaks for the photodecomposed products of comparable integration with those of CH_2Br_2 were observed in both the ^1H and ^{13}C NMR spectra (Figure 1d). The concentration of Br_2 steadily increased with the photoirradiation time (Figure 1b) and was determined by UV/Vis spectroscopy to be 0.92 M after 3 hours by reference to a standard solution of Br_2 in CH_2Br_2. The change in absorbance upon photoirradiation clearly decelerated under a flow of Ar, instead of O_2, thereby indicating that the oxidative photodecomposition of CH_2Br_2 actually accelerated the generation of Br_2, presumably owing to the formation of carbon oxides. Elemental Br_2, which has a boiling point of 58.8°C (neat), was condensed with a little vaporization in the solution by the photodecomposition of CH_2Br_2, but most of the other photodecomposed products with low boiling points, such as HBr and carbon oxides, could have escaped out of the system under a flow of O_2 at 40°C (Scheme 1, Equation (2)). HBr could actually be trapped by amines to form their corresponding HBr salts outside of the system (see below). The reactions may proceed through two possible mechanisms: the initial photolytic cleavage of a carbon–bromine bond (path a) or through the radical substitution of a hydrogen atom in CH_2Br_2 by the bromine radical (path b).[16] Subsequent reactions of the resulting halomethane radicals with oxygen would generate the corresponding peroxy radicals to give formaldehyde, formyl bromide, and bromophosgene in a Russell mechanism.[22] The carbonyl compounds that carry bromine atoms further decompose to give carbon monoxide and dioxide,

thereby resulting in an increase in Br_2 concentration in the system (Scheme 2). We expected that these reactions could also generate possible higher-brominated hydrocarbons owing to radical cross-coupling and bromination reactions of the halomethane radicals in the proposed mechanism. However, magnified NMR spectra (Figure 1d) indicated that the resulting sample solution only contained an extremely small amount of the higher-brominated $CHBr_3$, which had a chemical shift of $\delta = 6.83$ ppm. Hence, elemental Br_2 that was generated in the CH_2Br_2 solution was stable in the closed vessels at room temperature, tolerant of long-term storage, and available for use in a variety of applications.

The higher-brominated $CHBr_3$, which also existed as a liquid at room temperature, showed an analogous color change upon photoirradiation and the degree of photogeneration of Br_2 was more rapid compared with CH_2Br_2 (see the Supporting Information, Figure S2). The fully brominated methane, CBr_4, which exists as a solid, generated a brownish gas upon exposure to UV light, without any notable changes in its crystalline structure (see the Supporting Information, Figure S3). These brominated-methane compounds did not show the color change owing to Br_2 generation in common organic solvents, such as n-hexane, benzene, acetone, or simple alcohols, which were capable of reacting with Br_2 or reducing the radical photolysis of the carbon–bromine bonds. However, when solutions that contained the brominated methanes in CCl_4, $CHCl_3$, or CH_2Cl_2 were exposed to UV light, they showed the characteristic color changes owing to Br_2 generation. Representatively, the solutions of the brominated methanes in $CHCl_3$ after exposure to UV light for 1 hour showed stronger absorbance owing to Br_2 generation in the order CBr_4, $CHBr_3$, and CH_2Br_2 (Figure 2). The concentrations of Br_2 in sample solutions that were prepared from solutions of the brominated methanes (1 M) in $CHCl_3$ (10 mL) were approximately 0.80, 0.43, and 0.21 M, respectively. Thus, the chlorinated methane solvents may accelerate the photolysis of the carbon–bromine bonds, in harmony with their radical photolysis of the carbon–chlorine bonds.[13] As a control reaction, N-bromosuccinimide (NBS), which contains a N−Br bond that is

Scheme 2. Possible photodecomposition pathways of CH_2Br_2.

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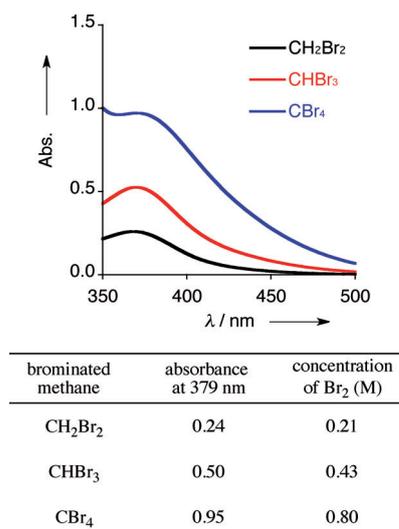| brominated methane	absorbance at 379 nm	concentration of Br₂ (M)
CH_2Br_2	0.24	0.21
$CHBr_3$	0.50	0.43
CBr_4	0.95	0.80

Figure 2. Absorption spectra (top) and the evaluated concentrations of Br₂ (bottom) of photodecomposed solutions of CH_2Br_2, $CHBr_3$, and CBr_4 in $CHCl_3$ measured upon 150-fold dilution with MeOH at 20 °C. The $CHCl_3$ solutions were exposed to UV light under a flow of O₂ at 40 °C for 1 h with a 20 W low-pressure mercury lamp.

Table 1. Bromination reactions of anisole with photodecomposed brominated methanes.[a]

Entry	Brominated methane	t [h][b]	Yield [%][c]	
			1Br	**1Br₂**
1	CH_2Br_2	0.5	93	–
2	CH_2Br_2	24	51	39
3	$CHBr_3$	0.5	90	–
4	CH_2Br_2 in $CHCl_3$	0.5	18	–
5	$CHBr_3$ in $CHCl_3$	0.5	65	–
6	CBr_4 in $CHCl_3$	0.5	65	21
7	CBr_4 in CH_2Cl_2	0.5	17	–

[a] Reactions were carried out by using mixtures of anisole (1.5 mmol) and liquid brominated methanes (10 mL) or chlorinated methane solutions (10 mL) that contained brominated methane (10 mmol), which had been exposed to UV light with a 20 W low-pressure mercury lamp. [b] Stirring time after the addition of anisole. [c] Yield of isolated product; the distribution of the mono- and disubstituted products was determined by ¹H NMR spectroscopy.

weaker than that of a typical C–Br bond, also decomposed in $CHCl_3$ at 40 °C upon photoirradiation to generate Br₂ (see the Supporting Information, Figure S4); the concentration of Br₂ after 1 hour was approximately 0.26 M, which resulted from 52 % consumption of NBS. Although brominated methanes have the potential advantage over NBS of carrying multiple bromine atoms in a molecule, CBr_4 and $CHBr_3$ can actually generate larger amounts of Br₂ in the system and even CH_2Br_2 attained a comparable concentration to NBS.

Bromination Reactions of Anisole with Photodecomposed Brominated Methanes

These results for the photogeneration of Br₂ from brominated methanes were applied in the bromination of anisole **1** in photodecomposed neat liquids of CH_2Br_2 or $CHBr_3$, or solutions of the brominated methanes in $CHCl_3$. Anisole **1** (0.16 g, 1.5 mmol) was added directly into photodecomposed CH_2Br_2 (10 mL), which was prepared upon exposure to UV light under a flow of O₂ for 3 hours at 40 °C, and the sample solution was stirred at 20 °C. 4-Bromoanisole (**1Br**) was isolated in 93 % yield after stirring for 0.5 hours (Table 1, entry 1), whilst a mixture of compound **1Br** and dibromoanisole (**1Br₂**) were obtained in 51 % and 39 % yield, respectively, upon prolonging the reaction time to 24 hours (Table 1, entry 2). When an excess amount of compound **1** was added into the solution of CH_2Br_2, the brownish color of the CH_2Br_2 solution, which originated from Br₂, immediately disappeared and compound **1Br** was obtained with the recovery of the unreacted substrate. A one-pot reaction, which was performed upon the direct photoirradiation of a solution of compound **1** in CH_2Br_2, decreased the yield of

the products to 67 % without recovery, presumably owing to the photodegradation of both the substrate and the products.[23] Moreover, the reactions in photodecomposed solutions of CH_2Br_2 that were prepared upon exposure to UV light under a flow of air or Ar instead of O₂ led to lower yields of 4-bromoanisole (40 % and 13 %, respectively); these results can be reasonably explained by the deceleration in the generation of Br₂, as described above.

Liquid $CHBr_3$, which can rapidly generate a large amount of Br₂ upon photoirradiation, also allowed the monobromination of anisole in 90 % yield under essentially identical conditions (Table 1, entry 3). Furthermore, the bromination reactions also occurred with photodecomposed solutions of CH_2Br_2, $CHBr_3$, or CBr_4 in $CHCl_3$ or CH_2Cl_2. When anisole (0.16 g, 1.5 mmol) was added into solutions of the brominated methane (6.7 equiv, 10 mmol) in $CHCl_3$ (10 mL) that had been exposed to UV light under a flow of O₂ for 3 hours, only 4-bromoanisol was obtained from CH_2Br_2 and $CHBr_3$ in 18 % and 65 % yield, respectively (Table 1, entries 4 and 5, respectively). Moreover, a 3:1 mixture of the mono- and dibrominated products were obtained in a combined 86 % yield with a solution of CBr_4 in $CHCl_3$ (Table 1, entry 6). From the UV/Vis spectra of the series of brominated methanes in $CHCl_3$ after photoirradiation (Figure 2), the observed yields of the bromination reactions mainly depended on the amount of Br₂ that was generated in the reaction systems. As expected from our above hypothesis, the radical species that were generated from chlorinated methane solvents under exposure to UV light accelerated the photodecomposition of the brominated methanes, only 17 % yield of 4-bromoanisole was obtained with a photoirradiated solution of CBr_4 in CH_2Cl_2, whose solvent had a higher stability under UV light (Table 1, entry 7).

Here, one must notice that the these decomposed chloromethane solutions need careful handling because they con-

tain extremely toxic phosgene (COCl$_2$) together with other inorganic products, such as Cl$_2$ and HCl, which may bring about unexpected side-reactions.[13, 24] However, the corresponding bromophosgene (COBr$_2$) is known to be unstable and thus likely to decompose immediately at room temperature or under exposure to light to produce Br$_2$, as well as carbon oxides (Scheme 2).[25–28] To avoid chemical hazards, as well as unexpected side-reactions in synthetic applications (see below), the neat liquid brominated methanes may be highly preferred in a variety of applications.

General Synthesis of Organobromine Compounds with Photodecomposed CH$_2$Br$_2$

We have demonstrated the bromination reactions of a variety of compounds that are capable of reacting with Br$_2$ in photodecomposed CH$_2$Br$_2$ (Table 2). These reactions were carried out by the addition of 1.5 mmol of the substrate into photodecomposed CH$_2$Br$_2$ (10 mL) that was prepared upon exposure to UV light with a 20 W low-pressure mercury lamp at 40 °C for 1 hour or 3 hours and the reaction was monitored by TLC and/or HPLC. Veratrol (**2**) allowed the monobromination at the 4-position to give product **2**Br in 93 % yield with the solution that was prepared upon exposure to UV light for 1 hour, but dibromination at the 4,5-positions occurred to give product **2**Br$_2$ in 99 % yield with the solution that was prepared upon prolonged photoirradiation for 3 hours (Table 2, entry 1). Compared with the reaction of compound **1**, methyl *p*-anisate (**3**), which contained an electron-withdrawing methyl ester group, slowly underwent bromination at the 3-position to give only the monobrominated product in 83 % yield (Table 2, entry 2). Anthracene **4** quantitatively gave dibrominated products (Table 2, entry 3). Although non-substituted five-membered heterocyclic pyrrole and furan gave turbid complicated reaction mixtures in photodecomposed CH$_2$Br$_2$, probably owing to oxidation reactions, thiophene (**5**) and 2,3,4-trisubstituted pyrrole **6** afforded their corresponding dibromination and α-bromination products in 83 % and 78 % yield, respectively (Table 2, entries 4 and 5). Acetanilide **7** underwent bromination at the 4-position of the phenyl ring and nitrogen atom of the amide group to give the dibrominated product in 93 % yield (Table 2, entry 6).

The photochemically generated Br$_2$ in the CH$_2$Br$_2$ solution also brought about the bromination of alkenyl compounds. 1-Decene (**8**) allowed the dibromination reaction in 97 % yield, whilst (*Z*)-cyclooctene (**9**) produced *trans*-1,2-dibromocyclooctane in 89 % yield (Table 2, entries 7 and 8, respectively). (*E*)-Stilbene (**10**) also underwent dibromination to give mixtures of the *anti*-adducts with *meso*-configurations and the thermally more-stable racemic (1*S*,2*S*) and (1*R*,2*R*) isomers in 15 % and 52 %, respectively, in the initial stage of the reaction (Table 2, entry 9). The reaction proceeded with an accompanying isomerization step to give only the latter racemic isomers in 82 % yield by prolonging the reaction time to 10 hours. Alkynyl compounds, such as 1,4-butynediol (**11**) and *p*-ethynyltoluene (**12**), also allowed

the addition of Br$_2$ to the triple bonds, thereby affording the dibrominated adduct in 76 % yield and a 5:1 mixture of the di- and tetrabrominated compounds in a combined 98 % yield (Table 2, entries 10 and 11). α-Bromination reactions occurred upon the addition of carbonyl compounds into the photodecomposed liquid CH$_2$Br$_2$. Acetophenone (**13**) gave a dibromination product in 97 % yield and dibenzoylmethane (**14**) also predominantly underwent dibromination at the α-carbon atoms (Table 2, entries 12 and 13, respectively). Furthermore, the addition of toluene (**15**) to the photodecomposed CH$_2$Br$_2$ solution gave benzyl bromide (**15**Br) in 75 % yield, together with a small amount of dibrominated **15**Br$_2$ in 4 % yield, as reported previously in the radical bromination reaction of toluene with Br$_2$ (Table 2, entry 14).[29, 30]

Oxidative Bromination Reactions of Aniline and Phenol Derivatives

The addition of aniline (**16**) into photodecomposed CH$_2$Br$_2$ afforded a turbid, complicated reaction, most likely owing to its oxidation and condensation in the acidic media, whereas *p*-toluidine (**17**), which contained a methyl group at the 4-position, predominantly afforded the 2,6-dibrominated compound (**17**Br$_2$) in 37 % yield, together with tetrabrominated azotoluene (**17**Br$_2$)$_2$ in 14 % yield (Table 3, entries 1 and 2, respectively; also see the Supporting Information, Figure S5). Because *p*-toluidine (**17**) is known to cause an oxidative coupling reaction to form azotoluene, the formation of compound (**17**Br$_2$)$_2$ is reasonable in this reaction system.[31] Notably, we could not find the formation of any of the urea derivatives, which was a possible side-product if COBr$_2$ had formed (Scheme 2);[32] COBr$_2$ was detected by GCMS (Figure 1 c) in the photodecomposition of CH$_2$Br$_2$. These results, together with the ^{13}C NMR study (Figure 1 d), indicated that the photodecomposed CH$_2$Br$_2$ solution contained very little COBr$_2$, probably owing to its instability as described above (Scheme 2).

On the other hand, similar to the case of anisole (**1**; Table 1, entry 1), phenol (**18**) gave 2,4-dibromophenol in 93 % yield (Table 3, entry 3). 2,4-Di-*tert*-butylphenol (**19**) underwent a monobromination reaction at the 6-position to give compound **19**Br in 62 % yield, but 4,6-dibrominated **19**Br$_2$, which had an oxidized dienone structure, was also obtained in 28 % yield (Table 3, entry 4). The structure of compound **19**Br$_2$ was determined by spectroscopic measurements and by single-crystal X-ray crystallography. In the single-crystal structure, the 6-membered ring included an sp^3 carbon at the 4-position and C2=C3, C5=C6, and C1=O1 double bonds with lengths 1.32, 1.32, and 1.22 Å, respectively (Figure 3).[33] Because the isolated **19**Br was successfully converted into **19**Br$_2$ in 93 % isolated yield when it was added into photodecomposed CH$_2$Br$_2$ and stirred at 20 °C for 4 hours, compound **19**Br$_2$ was most likely formed through the temporal formation of **19**Br.

Control Bromination Reactions with Elemental Br$_2$

To assess the reactivity of Br$_2$ in the solutions of photodecomposed CH$_2$Br$_2$, we performed control reactions of compounds **1**, **3**, **10**, and **13** (1.5 mmol) by mixing with elemental Br$_2$ in CH$_2$Br$_2$ without photoirradiation (Scheme 3). For an accurate evaluation, a solution of Br$_2$ in 1 M CH$_2$Br$_2$ (10 mL) was prepared for all of the reactions wherein the amount of

Table 2. Synthesis of organobromine compounds with photodecomposed CH$_2$Br$_2$ solutions.[a]

Entry	Substrate	Products		t [h] Photoirradiation	Stirring[b]	T [°C]	Yield [%][c]
1	**2**	**2Br**	**2Br$_2$**	1 3	1 1	50 50	**2Br**: 93 **2Br$_2$**: 4 **2Br**: 0 **2Br$_2$**: 99
2	**3**			3	12	40	83
3	**4**			3	2	20	99
4	**5**			3	2	20	83
5	**6**			3	2	20	78
6	**7**			3	2	40	93
7	**8**			3	2	20	97
8	**9**			3	2	0	89
9	**10**	*meso*-**10Br$_2$**	*rac*-**10Br$_2$**	3 3	2 10	20 20	*meso*: 15 *rac*: 52 *meso*: 0 *rac*: 82
10	**11**			1	1	40	76
11	**12**	**12Br**	**12Br$_2$**	1	1	40	**12Br**: 81 **12Br$_2$**: 17
12	**13**			3	2	0	97
13	**14**	**14Br**	**14Br$_2$**	3	2	20	**14Br**: 17 **14Br$_2$**: 73
14	**15**	**15Br**	**15Br$_2$**	3	6	20	**15Br**: 75 **15Br$_2$**: 4

[a] Reactions were carried out upon mixing 1.5 mmol of substrate and photodecomposed CH$_2$Br$_2$ (10 mL), which was prepared upon exposure to UV light with a 20 W low-pressure mercury lamp at 40 °C. [b] Stirring time after the addition of the reaction substrates. [c] Yield of isolated product; the distribution of the mono- and disubstituted products was determined by ^{1}H NMR spectroscopy.

Table 3. Bromination reactions of aniline and phenol derivatives in solutions of photodecomposed CH_2Br_2.[a]

Entry	Substrate	Products	t [h] Photoirradiation	Stirring[b]	Yield [%][c]
1	**16**	complicated mixture	3	1	–
2	**17**	**17**Br$_2$ (**17**Br$_2$)$_2$	3	1	**17**Br$_2$: 37 (**17**Br$_2$)$_2$: 14
3	**18**		3	2	93
4	**19**	**19**Br **19**Br$_2$	3	2	**19**Br: 62 **19**Br$_2$: 28

[a] Reactions were carried out at 20 °C upon mixing the substrate (1.5 mmol) and photodecomposed liquid CH_2Br_2 (10 mL), which was prepared upon exposure to UV light with a 20 W low-pressure mercury lamp at 40 °C. [b] Stirring time after the addition of the substrates. [c] Yield of isolated product; the distribution of the mono- and disubstituted products was determined by ^{1}H NMR spectroscopy.
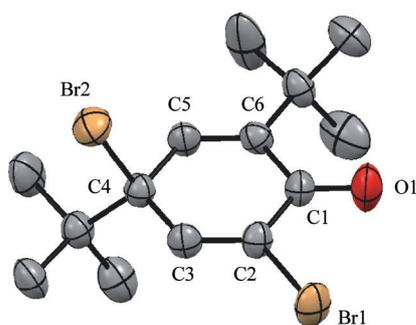

Figure 3. ORTEP of **19**Br$_2$. Ellipsoids set at 50 % probability, hydrogen atoms are omitted for clarity.[33]

Br_2 in the absorption spectra was approximately the same as that prepared from CH_2Br_2 upon exposure to the light for 3 hours at 40 °C. Interestingly, the observed brominated products and the yields of the control reactions were similar to the reactions in photodecomposed CH_2Br_2, thus indicating that the elemental Br_2 that was generated by photoirradiation actually kept its reactivity in the resulting CH_2Br_2 solution. However, the small differences that appeared in the ratios of the mono- and dibrominated products in the reaction of compound **1** and between the *meso-* and racemic isomers in the reaction of compound **10** (Scheme 3a versus Table 1, entry 1, and Scheme 3c versus Table 2, entry 9, respectively) indicated that other photodecomposed products, such as HBr, contributed to the reactions. Because electron-withdrawing groups decreased the reactivity of the attached phenyl ring for the electrophilic substitution of Br_2, compound **1** in the photodecomposed CH_2Br_2 solution might decrease the electron density of the phenyl ring through weak interactions of the alkoxide group with H$^+$ ions.[34] On the

other hand, dibrominated stilbene (**10**Br$_2$) in the photodecomposed CH_2Br_2 likely accelerated the structural rearrangement from *meso*-**10**Br$_2$ into a thermally stable *rac*-**10**Br$_2$ in the presence of HBr.[35]

Bromination Reactions with HBr in Photodecomposed CH_2Br_2

Because the solution of photodecomposed CH_2Br_2 not only contains Br_2 but also saturated HBr, it should also be applicable to acid-catalyzed bromination reactions with HBr. A substitution reaction of a hydroxy group of a tertiary alcohol with a bromine atom has been known to occur with HBr through an S_N1 mechanism. When 1-adamantanol (**20**) was added into a solution of photodecomposed CH_2Br_2 and stirred under reflux for 10 hours, the hydroxy group was successfully converted into a bromine group to give compound **20**Br in 99 % yield (Scheme 4, top). However, cyclohexanol (**21**), a secondary alcohol, upon addition into a solution of photodecomposed CH_2Br_2, underwent mono- and dibromination to provide compounds **21**Br and *trans*-**21**Br$_2$ in 49 % and 31 % yield, respectively (Scheme 4, bottom). These reactions can be explained by an acid-catalyzed mechanism owing to the generation of HBr by the photodecomposition of CH_2Br_2, as well as the possible radical-bromination reactions of CH_2Br_2 by the photochemically generated Br_2. In the reaction of compound **20**, initial dehydration catalyzed by H$^+$ ions may allow the formation of a tertiary carbocation and subsequent addition of Br$^-$ would result in the formation of compound **20**Br. In the reaction of compound **21**, a similar dehydration step may initially occur to generate a secondary carbocation for the formation of a double bond in the cyclic ring; subsequent addition of Br_2 into the double bond gives dibrominated compound *trans*-**21**Br$_2$.
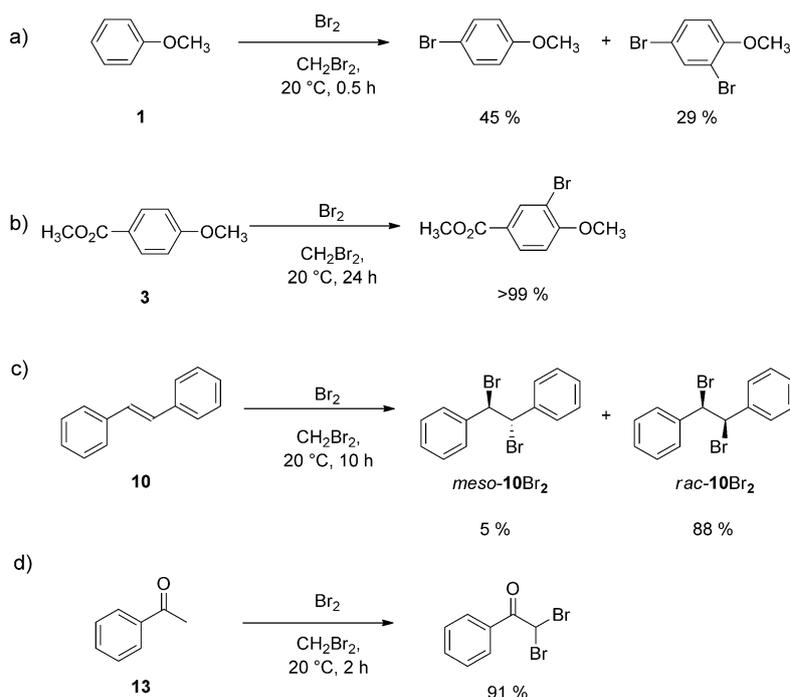
Scheme 3. Control bromination reactions of compounds **1**, **3**, **10**, and **13** with liquid Br₂.
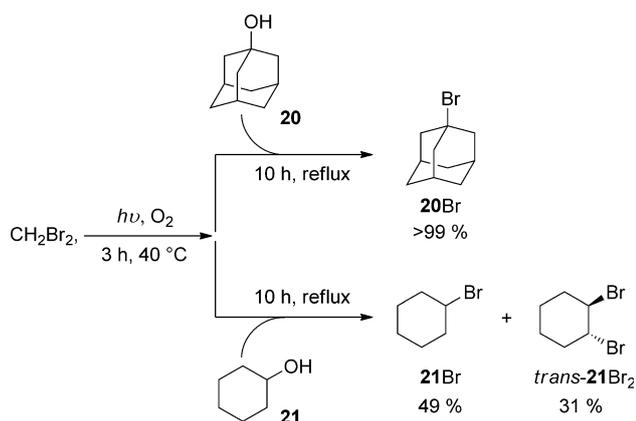
Scheme 4. Bromination reactions of compounds **20** and **21** in photodecomposed CH₂Br₂.

On the other hand, considering the bromine-atom economy, the vaporized HBr should also be useful for other reactions, such as the formation of the HBr salts of amines. We also found that the HBr salts of amines were efficiently obtained by using the photodecomposed gas of CH₂Br₂ outside of the photoreaction system. For example, the exposure of 1.0 mmol solutions of triethylamines in MeOH to photodecomposed CH₂Br₂ gas for 5 hours actually provided their corresponding HBr salts in 88 % yield.
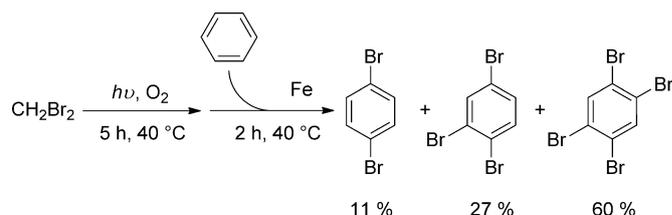
### Iron(III)-Catalyzed Bromination Reactions in Photodecomposed CH₂Br₂

Because the solution of photodecomposed CH₂Br₂ includes Br₂ without any notable chemical contamination, this solution was also applicable to iron(III)-catalyzed bromination

reactions. No bromination reaction of benzene was observed in photodecomposed CH₂Br₂ at 40 °C. However, when 1.2 equivalents of iron powder was added into the solution and the mixture was stirred for 2 hours, 1,4-dibromobenzene, 1,2,4-tribromobenzene, and 1,2,4,5-tetrabromobenzene were obtained in 11 %, 27 %, and 60 % yield, respectively (Scheme 5; also see the Supporting Information, Figure S6). This result indicates that iron in photodecomposed CH₂Br₂ is actually converted into FeBr₃ through a reaction with Br₂ and brings about the catalytic bromination reactions of benzene in the solution.[3f,36,37]

Multiple Bromination Reactions of Large Aromatic Compounds

Large disk-shaped aromatic compounds, such as hexaphenylbenzene (HPB) and metalloporphyrin derivatives that don't contain lipophilic substituents, generally have poor solubility into organic solvents, whereas they show relatively higher solubility into halomethane solvents. Thus, these solutions of photodecomposed brominated methane are considered to be suitable as a medium for bromination reactions. It has been known that HPB allows hexabromination in neat Br₂ and *meso*-substituted metalloporphyrins also undergo octabromination in CHCl₃ solutions that contain Br₂.[38,39] When we carried out the reaction of HPB with photodecomposed CH₂Br₂, which was prepared upon exposure to UV light for 6 hours at 40 °C, the multibromination reaction proceeded very slowly under reflux conditions. To increase the concentration of Br₂ in the reaction system, we chose CHBr₃ as a solvent. HPB was successfully converted into the hexabrominated form of hexakis(4-bromophenyl)benzene as the sole product in 86 % yield in photodecomposed CHBr₃, which was prepared upon exposure to UV light for 6 hours at 40 °C, by heating at reflux for 7 days (Scheme 6,

Scheme 5. Iron(III)-catalyzed bromination reaction of benzene in photodecomposed CH₂Br₂.

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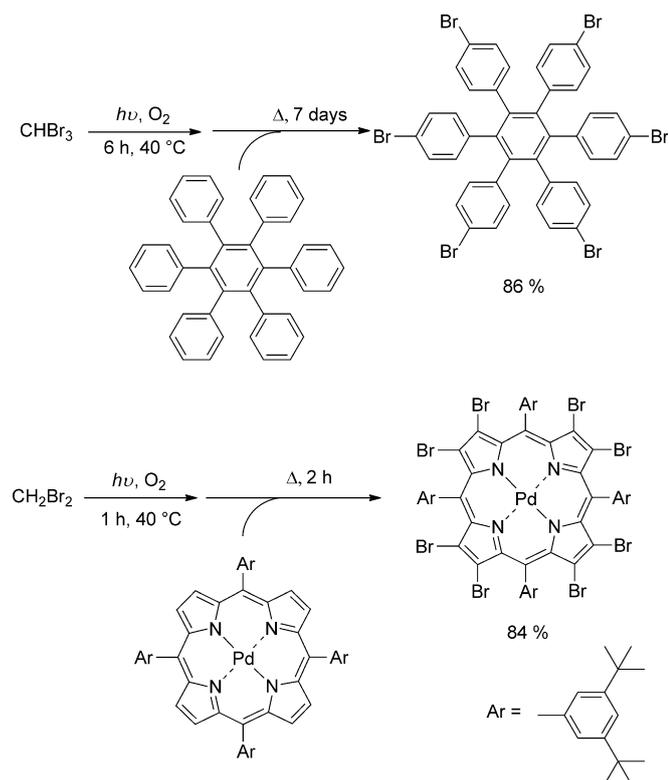
Scheme 6. Bromination reactions of hexaphenylbenzene and Pd^{II}–porphyrin in photodecomposed CH_2Br_2.

Figure 4. Photochemical bleaching of red rose petals with CH_2Br_2. a) Before (left) and after (right) exposure of the rose petal to UV light in CH_2Br_2 (1 mL) for 10 min at 20 °C under a flow of O_2 with a 20 W low-pressure mercury lamp. b) Chemical structure of rose anthocyanin. c) A cross-shape appeared on a rose petal through painting with liquid CH_2Br_2 and subsequent UV irradiation.

top). Moreover, a solution of 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato palladium(II) in photodecomposed CH_2Br_2 allowed octabromination at the pyrrole β-positions in 84% yield by heating at reflux for 2 hours (Scheme 6, bottom).

Photochemical Bleaching of Colored Natural Plants

Radical reagents, such as H_2O_2 and 2,2′-azobis-2-methyl-propanimidamide dihydrochloride (AAPH), have been known to bleach colored natural materials.[40] Finally, we demonstrated the photochemical bleaching of flower petals by the photochemical generation of Br_2 from liquid CH_2Br_2. A red rose petal was immersed in a solution of CH_2Br_2 (1 mL) and exposed to UV light under a flow of O_2 at 20 °C for 10 min. The red color of the rose became gradually decolorized upon photoirradiation, but no change was observed without CH_2Br_2 or photoirradiation (Figure 4a). Decolorization also occurred when the petal was immersed directly in photodecomposed CH_2Br_2. Thus, Br_2 that is generated in photodecomposed CH_2Br_2 most likely brings about the observed decolorization of the rose petal. It is well-known that the color of the rose petals originates from an anthocyanin dye that is composed of a chromophoric flavylium ion and hydrophilic sugar components (cyanidine 3,5-*O*-diglucoside; Figure 4b).[41–43] Oxidation of the flavylium ions, which contain multiple hydroxy groups, allows cleavage of the C=O$^+$ bond of the benzopyrylium ring and/or formation
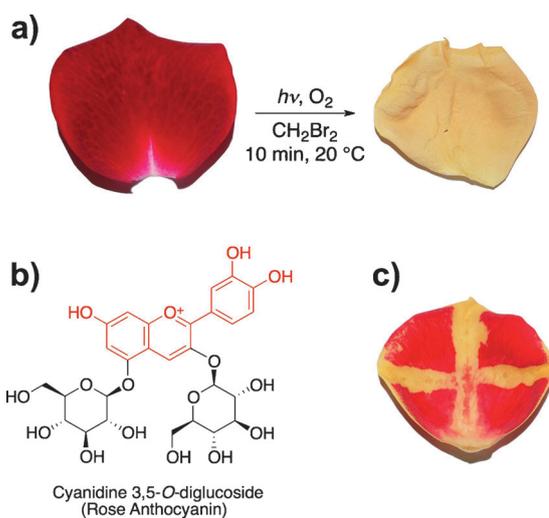
of quinoidal structures, which are highly dependent on the environmental pH value, thereby resulting in color changes or bleaching.[44] As one can expect from the oxidative bromination reaction of compound **19** in photodecomposed CH_2Br_2, which afforded dienone **19**Br_2 (Table 3, entry 4), the radical oxidation of the flavylium ions owing to Br_2 is one of the plausible pathways to decolorize the anthocyanin dye. Because Br_2 can form HOBr, a strong oxidant, in water, HOBr may also contribute to the oxidation of the anthocyanin molecules in the petal.[45] Then, by taking advantage of CH_2Br_2, a photoresponsive liquid-chemical storage of Br_2, we succeeded in drawing on the petal. Crossed lines were painted on the petal with CH_2Br_2 and the petal was subsequently exposed to UV light under a flow of O_2. The painted area was gradually bleached and clear crossed lines appeared as shown in Figure 4c. The liquid CH_2Br_2 that was adsorbed onto the surface or penetrated into the petal may generate Br_2 upon exposure to the light, thereby resulting in the local oxidation of the anthocyanin molecules that are involved in the painted area.

Conclusions

In this study, we have reported the photochemical generation of elemental Br_2 from brominated methanes upon photoirradiation with a 20 W low-pressure mercury lamp and successfully used these events in organic synthesis and in materials science. Despite the low electric power of the lamp, the brominated methanes, such as CH_2Br_2, can efficiently decompose to give Br_2 with the vaporization of carbon oxides, as well as HBr, upon simple UV irradiation. The liquid brominated methanes can be used not only as or-

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ganic solvents but also for the photoresponsive molecular storage of Br$_2$, wherein the amount and situations of Br$_2$ generation are photochemically controllable. By taking advantage of the in situ generation of Br$_2$ from the organic solvent itself without any notable chemical contamination of the system, many organobromine compounds can be conveniently synthesized in high practical yields with or without the addition of a catalyst, wherein Br$_2$ that is generated in CH$_2$Br$_2$ maintains its potential reactivity for the bromination reactions. As one of the characteristic features of the reactions with photodecomposed CH$_2$Br$_2$, the generated HBr is available as a reagent for various reactions, such as the substitution of a hydroxy group, salt formation, and working as an acid catalyst. Furthermore, liquid CH$_2$Br$_2$ shows the area-selectable photochemical bleaching of dye molecules that are involved in natural plants. Although the liquid brominated methanes, especially CH$_2$Br$_2$, have been mainly used as organic solvents, this study presents a new potential function of the brominated methanes in the photoresponsive molecular storage of elemental Br$_2$, which will furnish great technical benefits, as well as scientific advancements, in a wide variety of applications.

Experimental Section

Materials

Unless otherwise stated, all reagents and solvents were used as received. 1,2-Dimethoxybenzene ($>99\%$), anthracene ($>97\%$), cyclooctene ($>95\%$), acetophenone ($>98.5\%$), and 2,4-di-*tert*-butylphenol ($>97\%$) were purchased from Tokyo Kasei Co., Ltd. (TCI). Dibromomethane ($>98\%$), tetrabromomethane ($>98\%$), aniline ($>99\%$), thiophene ($>98\%$), 2-butyn-1,4-diol ($>98\%$), 1-adamantanol ($>99\%$), benzene ($>99\%$), and Na$_2$S$_2$O$_3$·5H$_2$O ($>99\%$) were purchased from Nacalai Tesque, Inc. Bromoform ($>97\%$), bromine ($>99\%$), methyl *p*-anisate ($>98\%$), acetanilide ($>99\%$), 1-decene ($>95\%$), *E*-stilbene ($>98\%$), *p*-ethynyltoluene ($>97\%$), dibenzoylmethane ($>98\%$), toluene ($>99\%$), *p*-toluidine ($>98\%$), phenol ($>99\%$), iron powder (-150 μm, $>99.9\%$), hexaphenylbenzene ($>98\%$), cyclohexanol ($>99\%$), anhydrous NaHCO$_3$ ($>99.5\%$), and anhydrous Na$_2$SO$_4$ ($>99\%$) were purchased from Wako Pure Chemical Industries Ltd. CHCl$_3$ ($>99\%$) was purchased from Kishida Chemical Co. Ltd. Trisubstituted pyrrole **6** and 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato palladium(II) were synthesized according to literature procedures.[46,47] Bromoform, including a stabilizer (about 10–20 vol.% EtOH), was washed with water and dried over Na$_2$SO$_4$ and then freshly distilled under low pressure prior to use. Most of the brominated products were unambiguously characterized by ^{1}H NMR and IR spectroscopy with reference to the previous studies and the Aldrich FTNMR and FTIR Libraries (ver. 4.0). New compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, MS (FAB), elemental analysis, and X-ray diffraction.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 spectrometer (400 MHz for ^{1}H nuclei and 100 MHz for ^{13}C nuclei) or on a Bruker AVANCE 500 spectrometer (500 MHz for ^{1}H nuclei). Chemical shifts (δ) are reported in ppm with respect to tetramethylsilane or CDCl$_3$ as the internal standard. Electronic absorption spectra were recorded on a JASCO type V-670 UV/VIS/NIR spectrometer that was equipped with a JASCO type ETC-717 temperature/stirring controller. IR absorption spectra were recorded on a JASCO FT/IR-4200 Fourier transform infrared spectrometer. MS (FAB) was performed on a JEOL JMS-BU30 LC Mate spectrometer with 3-nitrobenzylalcohol as the matrix. Elemental

analysis was performed on a YANACO CHN Corder MT-5. X-ray diffraction data were collected on a Bruker SMART APEX II Ultra CCD diffractometer by using Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 298 K. An empirical absorption correction was applied by using the SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares calculations on $F2$ by using the SHELXTL 97 program package.[48] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added to the calculated positions. The packing diagrams were drawn by using ORTEP-3. GCMS was performed on a Thermo Scientific TRACE GC Ultra spectrometer that was equipped with a Thermo Scientific ISQ single-quadrupole mass spectrometer and a Thermo Scientific TG-SQC capillary column (15 m × 0.25 mm × 0.25 μm) and He as the carrier gas.

Typical Procedure for Bromination Reactions

A cylindrical flask (42 mm) was equipped with a 30 mm quartz-glass jacket at the center of the flask, including a low-pressure mercury lamp, and charged with CH$_2$Br$_2$ (10 mL). The solution was stirred vigorously in a flow of O$_2$ at 40 °C under photoirradiation for 1–3 h. After the photoirradiation, the substrate (1.5 mmol) was added into the solution and the mixture was stirred for 0.5–12 h at 0–50 °C. After the reaction, the sample solution was mixed with aqueous NaHCO$_3$ under vigorous stirring. The organic layer was then washed with aqueous Na$_2$S$_2$O$_3$ (2 %) and water. The sample solution was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness to give the brominated products.

Bromination of Hexaphenylbenzene (HPB)

A cylindrical flask (42 mm) was equipped with a 30 mm quartz-glass jacket at the center of the flask, including a low-pressure mercury lamp, and charged with CHBr$_3$ (10 mL). The solution was stirred vigorously in a flow of O$_2$ at 40 °C under photoirradiation for 6 hours. After the photoirradiation, HPB (50 mg, 0.09 mmol) was added into the solution and the mixture was heated to reflux for 7 days. The sample solution after the reaction was evaporated to dryness. The residue was recrystallized with CHCl$_3$/*n*-hexane to give hexabrominated HPB as a white solid in 86 % yield (78.0 mg).

Bromination of 5,10,15,20-Tetrakis(3,5-di-tert-butylphenyl)porphyrinato palladium(II)

A cylindrical flask (42 mm) was equipped with a 30 mm quartz-glass jacket at the center of the flask, including a low-pressure mercury lamp, and charged with CH$_2$Br$_2$ (5 mL). The solution was stirred vigorously in a flow of O$_2$ at 40 °C under photoirradiation for 1 hour. After the photoirradiation, 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato palladium(II) (10 mg, 0.009 mmol) was added into the solution and the mixture was heated at reflux for 2 h. After the reaction, the sample solution was mixed with aqueous NaHCO$_3$ under vigorous stirring. The organic layer was then washed with aqueous Na$_2$S$_2$O$_3$ (2 %) and water. The sample solution was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness to give the octabrominated Pd^{II}–porphyrin as a deep-red solid in 84 % yield (13.6 mg).

Iron(III)-Catalyzed Bromination of Benzene

A cylindrical flask (42 mm) was equipped with a 30 mm quartz-glass jacket at the center of the flask, including a low-pressure mercury lamp, and charged with CH$_2$Br$_2$ (10 mL). The solution was vigorously stirred in flowing O$_2$ gas at 40 °C under photoirradiation for 5 hours. After the photoirradiation, benzene (1.5 mmol) and iron powder (100 mg, 1.8 mmol) were added into the solution, and stirred for 2 hours at 40 °C. After the reaction, the sample solution was mixed with aqueous NaHCO$_3$ under vigorous stirring. The organic layer was then washed with water. The sample solution was dried over anhydrous Na$_2$SO$_4$ and evaporated to dryness to give a mixture of 1,4-dibromobenzene, 1,2,4-tribromobenzene, and 1,2,4,5-tetrabromobenzenes in 11 %, 27 %, and 60 % yield, respectively (total weight: 520 mg).

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FULL PAPER

Photochemistry

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Akihiko Tsuda* ⎯⎯⎯⎯ ▮▮▮▮–▮▮▮▮

🖥 **Brominated Methanes as Photoresponsive Molecular Storage of Elemental Br$_2$**
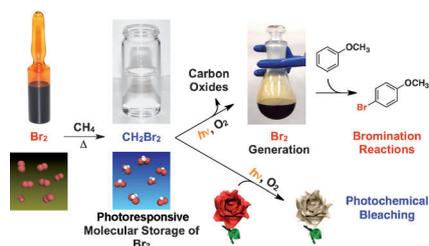
The generation of Br$_2$ from brominated methanes occurred upon photo-irradiation under O$_2$. The solutions that contained elemental Br$_2$ were useful for the synthesis of organobromine compounds and the macroscopic photochemical bleaching of colored plants.