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Graphical Abstract

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Synthesis of α,β-Dibromo Ketones by Photolysis of α-Bromo Ketones with N-bromosuccinimide: Photoinduced β-Bromination of α-Bromo Ketones

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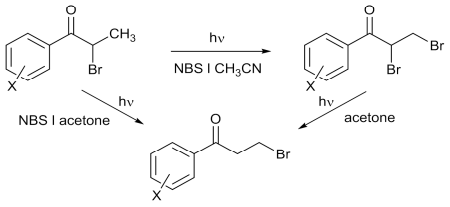
Da Yoon Moon, Sejin An and Bong Ser Park*
Department of Chemistry, Dongguk University(Seoul Campus), Seoul 04620, Korea



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Synthesis of α,β-Dibromo Ketones by Photolysis of α-Bromo Ketones with N-bromosuccinimide: Photoinduced β-Bromination of α-Bromo Ketones

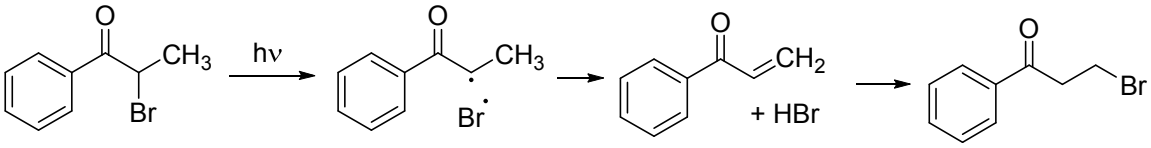
Da Yoon Moon, Sejin An and Bong Ser Park*
Department of Chemistry, Dongguk University (Seoul Campus), Seoul 100-715, Korea

Abstract: Irradiation of α-bromopropiophenones in the presence of NBS results in theformation of α,β-dibromopropiophenones, which can be viewed as β-bromination of α-bromopropiophenones. The reaction is believed to go through a series of reactions; photoinduced C-Br bond cleavage, elimination of HBr to give α,β-unsaturated ketone intermediates, and addition of Br_2, which are formed by the reaction between HBr and NBS. From mechanistic studies of the reaction, we have also found a very convenient method for α-debromination of the α,β-dibromopropiophenones which is by simple irradiation of the dibromo ketones in acetone or 2-propanol without the use of any additives. Our results demonstrate that bromine can be added into or eliminated from the alpha, beta, or both positions to the carbonyl group by photochemical methods, which make synthetic options of bromine containing carbonyl compounds versatile.

1. Introduction

Bromination is undoubtedly one of the most important methods in organic functional group interconversion. Thus, various techniques for bromination have been developed from many different starting compounds.[1] Among them, there has recently been much interest over the preparation of α.β-dibromo carbonyl compounds because they serve as useful intermediates in organic synthesis. For example, dibromo compounds have been used as precursors for α-bromoacrylates,[2] vinyl azides,[3] β-nitro ketones,[4] indanones,[5] pyrazoles,[6] etc. Furthermore, a facile preparation method for the dibromo compounds is a key feature in using them as a protecting group in vinyl ketones.[7] The vicinal dibromides can also be used as UV photoacid generators for photoresist because photodecomposition of such compounds can provide a remarkably clean source of bromine atoms.[8] Even though the dibrominated compounds could be obtained easily by Br_2 addition to vinyl ketones,[9] the use of hazardous molecular bromine was unsuitable hence, there has been the need for more convenient and safer methods.[10]

Recently, we reported that α-bromopropiophenones could be converted into β-bromopropiophenones *via* photochemical C-Br bond cleavage reaction, which we coined as photoinduced 1,2-Br shift reaction.(Scheme 1)[11] It was suggested that the 1,2-Br shift occurred by conjugate addition of HBr into α,β-unsaturated ketone intermediates formed by the photoinitiated C-Br bond cleavage and disproportionation of the resulting radical pairs. We envisioned that the α,β-unsaturated ketone intermediates would be trapped by Br_2 to give α.β-dibromo ketones if the photolysis of α-bromopropiophenones is done under Br_2 enriched condition. It is known that Br_2 can be formed by the reaction of N-bromosuccinimde (NBS) with HBr.[12] Since HBr is one of initial photoproducts of the 1,2-Br shift reaction, we speculated that α.β-dibromo ketones would be formed when α-bromopropiophenones are irradiated in presence of NBS. The formation of the α,β-dibromo ketones from α-bromo ketones would be considered as a formal β-bromination, which is very rare in organic synthesis.[13] To our delight, β-bromination was observed to occur in a very effective way, which will be described below.

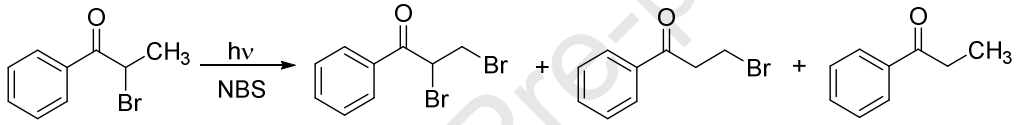


Scheme 1. Photoinduced 1,2-Br shift reaction.

2. Result and discussion

α-Bromopropiophenones, which were prepared by α-bromination of the corresponding propiophenones using $CuBr_2$, were irradiated as 0.02-0.03 M solution in the presence of NBS using a photolysis setup whose light source was a Pyrex filtered light of a 450W Hanovia medium pressure mercury arc lamp. The photolysis products were separated by column chromatography, whereby the structure of each product was characterized by routine spectroscopic analysis. To obtain the optimum condition for the photolysis reaction, reactant **1a** was chosen as the base compound and several solvents were tested shown in Table 1.

Table 1. Product distribution in photolysis of **1a** using various solvents



1a **2a** **3a** **4a**

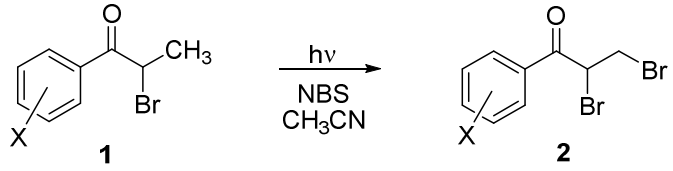
Solvent	Product Distribution (%)[a]		
	2a	**3a**	**4a**
Acetonitrile	100	-	-
Acetone	-	78	22
Benzene	81	19	-
Dichloromethane	59	41	-
Chloroform	38	52	10
Ethyl acetate	54	46	-

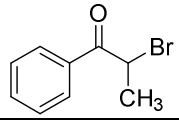
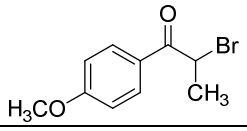
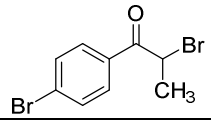
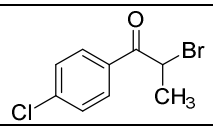
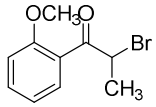
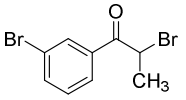
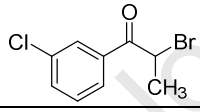
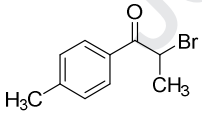
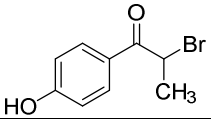
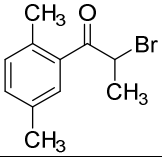
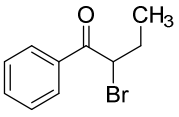
[a] The numbers were obtained by comparing integration of ^{1}H NMR signal of each product after irradiation until all the starting ketones disappeared. The photolysis was done in 0.025 M solution containing **1a** and NBS(1.1 equivalents).

It was observed that product distribution was strongly dependent on the type of solvents used. In acetonitrile, the β-bromination reaction product **2a** was formed exclusively, while the 1,2 bromine shift product **3a** became a major product in acetone. The product selectivity of **2a** over **3a** decreased in benzene by ca. 10% relative to the result in acetonitrile, and comparable amounts of **2a** and **3a** were obtained in other solvents such as dichloromethane, chloroform and ethyl acetate. In alcoholic solvents such as methanol and 2-propanol, a large amount of polymeric products were formed, whose structure could not be determined. The amount of NBS did not have a significant effect on product distribution, however, the product ratios seemed to be dependent on the irradiation time, which was due to photochemical reactions of **2a** under the given photolysis condition, *vide infra*. Since the product selectivity of **2a** was the best and the irradiation time dependence of the yield of **2a** was the smallest out of all the solvents tested, acetonitrile was chosen for the rest of the experiments.

With the optimum condition at hand, we investigated photochemical reactions of several compounds, as shown in Table 2.

Table 2. Product distribution in photolysis of various α-bromoalkyl phenyl ketones



Substrate		Product distribution (%)[b]		Yield of **2** [c] (%)
		2	Other Products	
1a		100	-	83(72)
1b		100	-	82(71)
1c		100	-	95(86)
1d		100	-	80(70)
1e		100	-	99(89)
1f		100	-	99(82)
1g		100	-	79(68)
1h		62	Benzylic bromination (38)	52
1i		-	Ring bromination[d](100)	-
1j		-	Benzylic bromination(100)	-
1k		90	Norrish/Yang photoreaction(10)	-[e]

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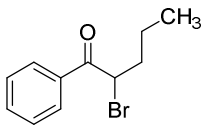
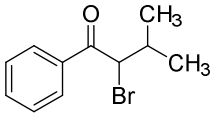
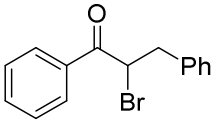
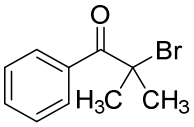
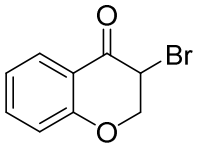
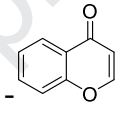
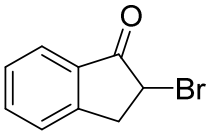
1l		75	Norrish/Yang photoreaction(25)	-[e]
1m		-	Polymeric products	(15)[f]
1n		100	-	75(55)[g]
1o		80	Tri-bromo product(20)	78(65)
1p		-	-  (100)	-
1q		100[h]	-	90[i]

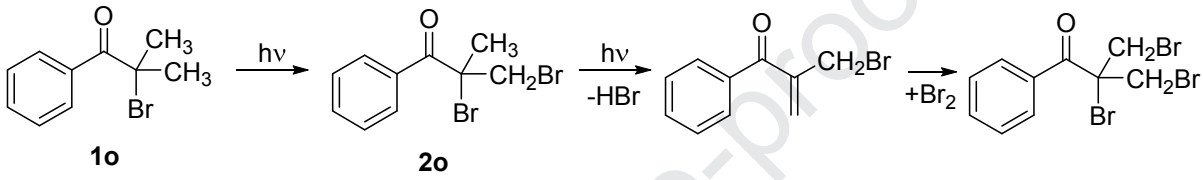
[a] Reaction condition: 0.025 M solution of **1** in acetonitrile, NBS(1.1 eq.) [b] Values obtained by integration of ^{1}H NMR. [C] The yields were determined by integration of ^{1}H NMR spectra using methyl benzoate as an internal standard. (In parenthesis are isolated yields. During the isolation, HBr elimination occurred in small extent in most cases.)
[d] It turned out to be a thermal reaction. [e] The yield was not determined because it was strongly dependent on irradiation time due to secondary photoreactions. [f] The relative yield using NMR integration could not be obtained due to broadness of the spectrum. [g] Only the *trans* product was detected and isolated. [h] *cis* : *trans*= 1 : 4. [i]The *cis* and *trans* isomers could not be separated.

The dibromo ketones **2** were obtained as a major product in good yields from photolysis of most ketones that we analyzed. In cases where one or more methyl substituents were present in a benzene ring such as **1h** and **1j**, benzylic bromination became a major competing pathway with the desired β-bromination. For **1i** containing a hydroxyl group in the benzene ring, both ortho positions to the hydroxy group were brominated, which turned out to be a thermal reaction later from further investigation. However, **1b** and **1e**, which have a methoxy group at either *para* or *ortho* position to the carbonyl, went through the desired β-bromination with no interference of other side reactions.
Other alkyl ketones apart from propiophenones, **1k** to **1q**, were also tested under the same reaction condition. For **1k** and **1l**, Norrish/Yang photoreaction[14] products were also formed, which made the reaction mixtures more difficult to analyze compared to other ketones. Apparently, the β-bromination reaction is slower than photoinduced 1,2-Br shift reaction because the Norrish/Yang products are not formed from photolysis of **1k** and **1l** in a given

reaction condition with no NBS present. As a reference, rates of the Norrish/Yang reaction of α-substituted phenyl alkyl ketones are known to be in the order of 10^8 s^{-1}.[15]

The yield of the desired β-bromination product from **1m** was further reduced mainly due to the formation of polymeric precipitates during the reaction. It can be speculated that the β-bromination of **1m** is hampered by steric hindrance caused by an extra methyl group at β position to the carbonyl, resulting to polymerization of the α,β-unsaturated ketone intermediate. Further characterization of the polymeric precipitates was nor carried out due to their insoluble nature.

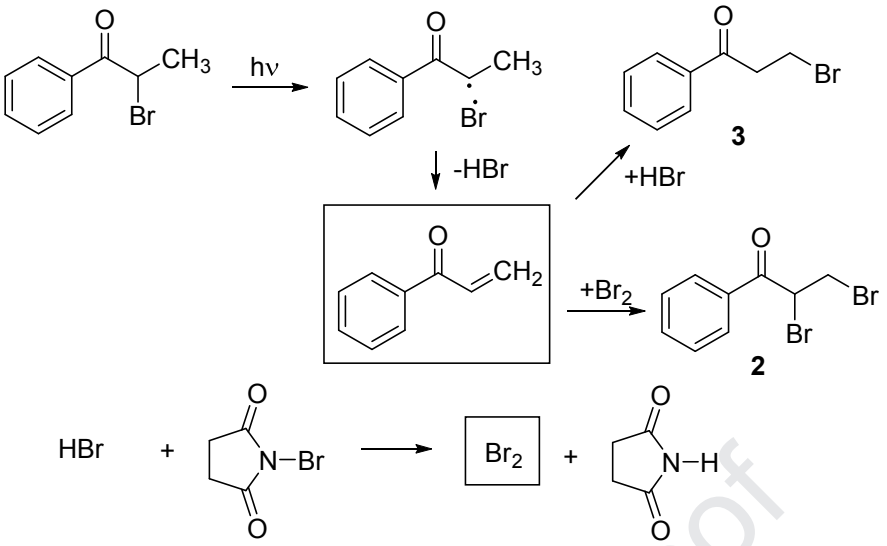
In photolysis of **1o**, the products from a secondary photoreaction were always contained in the reaction mixture. The initially formed β-bromination product seemed to go through the same reaction sequence as the first one, which was α C-Br bond cleavage, disproportionation, and Br_2 addition. The secondary photoreaction of the initial product occurred at the other methyl group of **1o** to form a tribromo ketone as shown in Scheme 2.



Scheme 2. Photochemical reaction of α-bromoisobutyrophenone (**1o**).

In the case of **1p**, chromone was the only product formed. Apparently, β-bromination reaction could not occur due to the stability of the chromone ring. In contrast, β-bromination reaction easily occurred during photolysis of an indanone derivative, **1q**.

Our proposed mechanism for the formation of β-bromination products as shown in Scheme 3 is similar to the one proposed for photoinduced 1,2-Br shift reaction of α-bromopropiophenones, except that Br_2 addition to α,β-unsaturated carbonyl intermediates becomes a predominant reaction pathway under the Br_2 enriched reaction condition whereby bromine molecules are formed by the reaction between NBS and HBr. One could argue that the dibromo ketones would be formed by α-bromination of initially formed β-bromo ketones under the influence of NBS. In fact, there have been a few reports showing photochemical α-bromination of ketones using NBS.[16] In order to get a better understanding of the reaction mechanism, we performed the photolysis of β-bromopropiophenone. Under the same reaction condition as described above, the ketone was essentially inert, which led us to exclude the α-bromination of β-bromo ketones from possible reaction mechanisms for the formation of β-bromination reaction products.



Scheme 3. Proposed mechanism for photochemical β-bromination of α-bromopropiophenones.

The reaction mechanism implies that the product ratios of **2** and **3** are determined by the relative concentration of Br_2 and HBr in solution, since they are derived from the same α,β-unsaturated ketone intermediates. In the presence of NBS, Br_2 addition to give **2** becomes the dominant reaction pathway, whereas the formation of **3** becomes the predominant reaction pathway in the absence of NBS. Even though the above reaction mechanism provides a reaction route to the observed dibromo ketones, their fate under photolysis condition remain doubtful, since they possess a photolabile alpha C-Br bond and therefore, could be involved in the reaction process. Can photolysis of **2** form the α,β-unsaturated ketone intermediate and convert it into **3**, if the reaction condition changes whereby the concentration of HBr exceeds that of Br_2? We may have already encountered such a case. Table 1 shows that the β-bromination reaction product **2a** is absent in the reaction mixture when photolysis is done in acetone. The result was obtained after complete conversion of the starting ketone, but further examination revealed that the dibromo ketone was in fact formed at an earlier stage of the reaction and significantly decreased with concomitant increase of **3a** as the photolysis continued. Figure 1 shows the irradiation time dependence of product ratios in photolysis of **1a** in acetone.

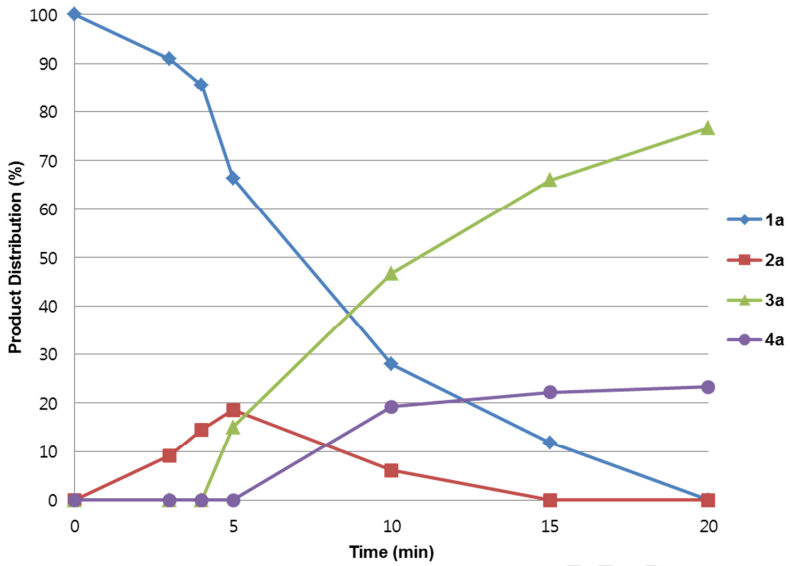
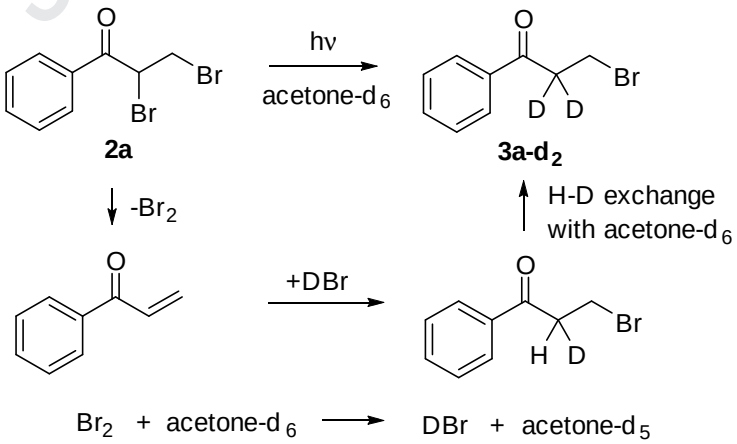


Figure1. Irradiation time dependence of product ratios in photolysis of **1a** in acetone.

The dibromo ketone **2a** was initially formed as a result of photolysis of **1a** in the presence of NBS, consequently, photolysis of **2a** under the same condition led to the formation of α.β-unsaturated ketone and Br_2 *via* the C-Br bond cleavage followed by disproportionation. The latter process is known to occur very fast, with rate constants exceeding 5 x 10^7 s^{-1}.[17] The bromine molecules produced at this stage reacted with acetone to form brominated acetone and HBr, which consequently added into the α.β-unsaturated ketone to form **3a** as observed in our experiment. To ascertain the accuracy of the mechanism, we irradiated **2a** in acetone-d_6 under the same reaction conditions and observed that **3a-d_2** was formed as the major product, as shown in Scheme 3. This suggests that the major product **3a** from photolysis of **1a** in acetone was probably formed from the secondary photoreaction of **2a**. Besides its mechanistic implication, the reaction can find useful application in α-debromination of α,β-dibromo carbonyl compounds without using any added reducing agents.

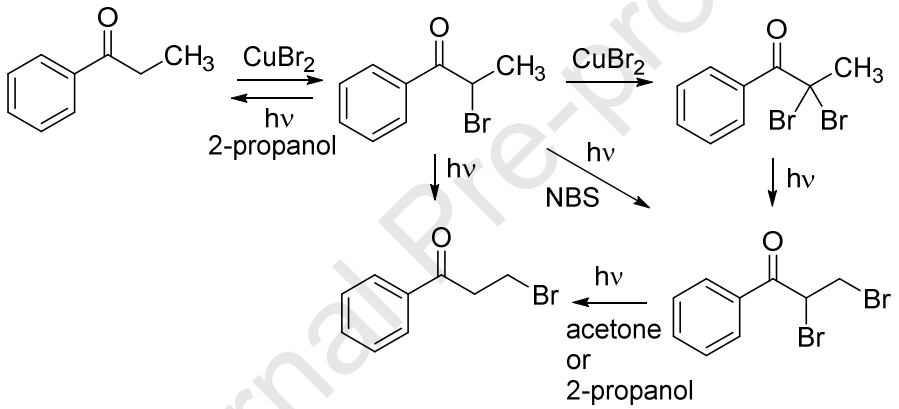


Scheme 3. Photoinduced α-debromination reaction of **2a**.

α-Debromination of **2** to form **3** can also be achieved if the acetone is replaced with 2-propanol as the solvent. The reaction in 2-propanol is photoreduction that is known to occur *via* radical chain mechanism, as discussed in our previous report.[18]

We have also tested whether the α,β-unsaturated ketone intermediate can be observed upon completion of photolysis in the presence of aniline where it can act as a quencher for Br_2.[19] When **2** was irradiated in acetonitrile in the presence of 1.2 equivalents of aniline, α,β-unsaturated ketone was obtained as the major product with a minimal amount of **3** formed. As mentioned above, the α,β-dibromo ketones have been utilized as a protecting group of vinyl ketones. The photochemical reaction of the dibromo ketones in the presence of aniline would be a valuable addition to other known methods.[20]

From our previous results showing that photolysis of α-bromopropiophenones leads to efficient conversion into β-bromopropiophenones, we envisioned that the α,β-dibromo compound **2** can also be prepared photochemically from α,α-dibromopropiophenones. To fulfil our expectation, photolysis of α,α-dibromopropiophenone gave the desired product **2** in good yields both in solution and neat condition. This reaction completes a valuable set of photochemical Br-shift reactions starting from α-bromopropiophenones, as shown in Scheme 4.



Scheme 4.Photochemical interconversion of various Br containing ketones.

3. Conclusions

In summary, photolysis of α-bromopropiophenones in acetonitrile in the presence of NBS resulted in the formation of α,β-dibromopropiophenones in good yields. The facile and eco-friendly reaction procedure, in which no hazardous chemical such as bromine was used, would provide a valuable addition to the known synthetic methods of the dibromo ketones. From studies on the reaction mechanism, we have also found a very efficient method for α-debromination of the α,β-dibromopropiophenones which is by simple irradiation of the dibromo ketones in acetone or 2-propanol without using any additives. Our results demonstrate that bromine can be added into or eliminated from alpha, beta, or both positions to the carbonyl group by photochemical methods, which make synthetic options of bromine containing carbonyl compounds versatile.

4. Experimental section

General Information

All reagents and solvents were purchased from commercial suppliers and were used without further purification. The starting materials, α-bromo ketones, were synthesized using the purchased reagents. The reaction was monitored by thin layer chromatography on silica gel

60 F_{254} plate (Merck, Darmstadt, Germany). Column chromatography was done on silica gel (BioSphere silica gel 60um 60A; BioMec, Seoul, South Korea) with dichloromethane and n-hexane. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Auto-Sampler-HR-MAS 500 MHz-NMR Spectrometry in $CDCl_3$. IR spectra were recorded on Functional Anal-ATR-FTIR Spectrometer (IdentifyIR® Portable FT-IR Spectrometer; Smiths Detection, London, United Kingdom). High-resolution massspectra (HR-MS) were acquired under fast atom bombardments (FAB) condition on a JMS-700 MStation (JEOL, Tokyo,Japan).

General experimental procedure

The α-bromo ketones tested for photolysis were prepared by $CuBr_2$ bromination of the corresponding ketones. The synthetic process has been described in our previous paper.[21] α-Bromo ketone (0.2 mmol) and N-bromosuccinimide (0.22 mmol) were dissolved in the solvent (8 ml). The reaction mixture was placed in a test tube, and it was degassed by charging Ar gas for a few minutes. Photolysis of the mixture was done by using a typical photolysis setup with a light source as a 450W Hanovia medium pressure mercury arc lamp filtered by Pyrex. The reaction was monitored by thin layer chromatography (TLC), and the irradiation continued until the α-bromo ketone could not be detected. Then the mixture was concentrated by a rotary evaporator at room temperature. The products were then purified through silica gel column chromatography (dichloromethane/hexane).

2,3-dibromo-1-phenylpropan-1-one (2a) [11]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.8, 7.4 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 5.40 (dd, *J* = 10.7, 4.1 Hz, 1H), 4.22 (dd, J = 10.7, 9.8 Hz, 1H), 3.80 (dd, J = 9.8, 4.1 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 134.5, 134.3, 129.2, 129.1, 41.5, 28.9 ppm.

2,3-dibromo-1-(4-methoxyphenyl)propan-1-one (2b)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.9 Hz, 4H), 6.98 (d, *J* = 8.9 Hz, 4H), 5.37 (dd, *J* = 10.7, 4.1 Hz, 1H), 4.22 (d, *J* = 10.7, 9.7 Hz, 1H), 3.89 (s, 6H), 3.79 (dd, *J* = 9.7, 4.1 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.4, 164.6, 131.6, 127.1, 114.4, 55.8, 41.5, 29.2 ppm; IR($CHCl_3$) 1677 cm^{-1} (C=O), HRMS (FAB+): m/z calcd for $C_{10}H_{11}{}^{79}Br_2O_2$ $[M+H]^+$: 320.9126, found: 320.9128.

2,3-dibromo-1-(4-bromophenyl)propan-1-one (2c)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 5.33 (dd, *J* = 10.7, 4.1 Hz, 1H), 4.21 (dd, *J* = 10.7, 9.8 Hz, 1H), 3.79 (dd, *J* = 9.8, 4.1 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.9, 133.0, 132.6, 130.6, 129.9, 41.3, 28.7 ppm; IR($CHCl_3$) 1691 cm^{-1} (C=O); HRMS (FAB+): m/z calcd for $C_9H_8{}^{79}Br_3O$ $[M+H]^+$: 368.8125, found: 368.8122.

2,3-dibromo-1-(4-chlorophenyl)propan-1-one (2d)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 5.34 (dd, *J* = 10.8, 4.1 Hz, 1H), 4.21(dd, J = 10.8, 9.8 Hz, 1H), 3.79 (dd, *J* = 9.8, 4.1 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.7, 141.1, 132.6, 130.5, 129.6, 41.4, 28.7 ppm; IR($CHCl_3$) 1690 cm^{-1} (C=O); HRMS (FAB+): m/z calcd for $C_9H_8{}^{79}Br_2{}^{35}ClO$ $[M+H]^+$: 324.8630, found: 364.8633.

2,3-dibromo-1-(2-methoxyphenyl)propan-1-one (2e)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.65 – 7.48 (m, 1H), 7.13-7.04 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.72 (dd, *J* = 10.4, 4.5 Hz, 1H), 4.20 (dd, *J* = 10.4, 9.8 Hz, 1H), 3.96 (s, 3H), 3.74 (dd, *J* = 9.8, 4.5 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.6, 159.0, 135.2, 132.3, 125.0, 121.4, 112.1, 56.0, 47.8, 29.8 ppm; IR($CHCl_3$) 1674 cm^{-1} (C=O); HRMS (FAB+): m/z calcd for $C_{10}H_{11}{}^{79}Br_2O_2$ $[M+H]^+$: 320.9126, found: 320.9127.

2,3-dibromo-1-(3-bromophenyl)propan-1-one (2f)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 6.2 Hz, 1H), 7.41 (dd, *J* = 7.8, 6.2 Hz, 1H), 5.33 (dd, *J* = 10.8, 4.0 Hz, 1H), 4.20 (dd, *J* = 10.8, 9.8 Hz, 1H), 3.79 (dd, *J* = 9.8, 4.0 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.6, 137.3, 136.0, 132.1, 130.7, 127.6, 123.5, 41.3, 28.6 ppm; IR($CHCl_3$) 1692 cm^{-1} (C=O); HRMS (FAB+): m/z calcd for $C_9H_8{}^{79}Br_3O$ $[M+H]^+$: 368.8125, found: 368.8122.

2,3-dibromo-1-(3-chlorophenyl)propan-1-one (2g)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 5.33 (dd, *J* = 10.7, 3.8 Hz, 1H), 4.20 (dd, *J* = 10.7, 9.6 Hz, 1H), 3.80 (dd, *J* = 9.6, 3.8 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.7, 135.8, 135.6, 134.4, 130.5, 129.2, 127.1, 41.3, 28.6 ppm; IR($CHCl_3$) 1689 cm^{-1} (C=O); HRMS (FAB+): m/z calcd for $C_9H_8{}^{79}Br_2{}^{35}ClO$ $[M+H]^+$: 324.8630, found: 324.8633.

2,3-dibromo-1-phenylbutan-1-one (2k)[22]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 5.38 (d, *J* = 10.6 Hz, 1H), 4.75 (dq, *J* = 10.6, 6.7 Hz, 1H), 2.03 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.7, 134.5, 134.3, 129.2, 129.1, 49.6, 45.1, 24.6 ppm.

2,3-dibromo-3-methyl-1-phenylbutan-1-one (2m)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 5.65 (s, 1H), 2.15 (s, 2H), 2.09 (s, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.5, 135.7, 134.0, 129.1, 128.9, 63.2, 53.6, 34.8, 31.2 ppm; IR($CHCl_3$) 1687 cm^{-1} (C=O); HRMS (FAB+): m/z calcd for $C_{11}H_{13}{}^{79}Br_2O$ $[M+H]^+$: 318.9333, found: 318.9331.

***trans*-2,3-dibromo-1,3-diphenylpropan-1-one (2n)[23]**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3, 1.1 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.60-7.50 (m, 4H), 7.47 – 7.35 (m, 3H), 5.84 (d, *J* = 11.3 Hz, 1H), 5.65 (d, *J* = 11.3 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.4, 138.5, 134.6, 134.4, 129.5, 129.2, 129.1, 129.1, 128.6, 50.0, 47.0 ppm.

2,3-dibromo-2-methyl-1-phenylpropan-1-one (2o)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 6.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.35 (d, *J* = 10.1 Hz, 1H), 3.90 (d, *J* = 10.1 Hz, 1H), 2.15 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 135.5, 132.7, 129.6, 128.6, 59.5, 38.9, 27.8 ppm; IR($CHCl_3$) 1687 cm^{-1} (C=O); HRMS (FAB+): m/z calcd for $C_{10}H_{11}{}^{79}Br_2O$ $[M+H]^+$: 304.9176, found: 304.9172.

Conflicts of interest

There are no conflicts to declare.

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*Simple and eco-friendly reaction procedure
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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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