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Solvent free, light induced 1,2-bromine shift reaction of α-bromo ketones

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ABSTRACT

Photolysis of α-bromopropiophenones in acetonitrile results in formation of β-bromopropiophenones with good product selectivity, which can be coined as 1,2-Br shift reaction. The product selectivity increases when the reaction is done in neat or solid state, where only the 1,2-Br shift product is formed in some cases. The reaction is suggested to proceed by C–Br bond homolysis to give a radical pair, followed by disproportionation and conjugate addition of HBr to the α,β-unsaturated ketone intermediate. When the unsaturated intermediate is stabilized by an extra conjugation, the reaction stops at the stage, in which the unsaturated ketone becomes a major product. The synthetic method described in this research fits in a category of eco-friendly organic synthesis nicely since the reaction does not use volatile organic solvents and any other additives such as acid, base or metal catalysts, etc. Besides, the method fits into perfect atom economy, which does not give any side products. The synthetic method should find much advantage over other alternative methods to obtain β-bromo carbonyl compounds.

1. Introduction

For a long time β-bromo ketones have been utilized as very important precursors to a broad range of intermediates in organic synthesis: enones, heterocyclic derivatives, 1,3-dicarbonyl compounds, etc. [1] Recently, the β-bromo ketones have also been used to synthesize β-azido carbonyl compounds which themselves have a variety of useful applications including DNA cleaving agents [2]. Even though synthetic methods for α-bromo ketones are numerous, only a limited number of methodologies to synthesize the β-bromo ketones can be found in the literature [3]. One reason for the relatively less known examples of the β-bromo ketone synthesis is that any drastic reaction conditions such as high temperature can easily lead to dehydrobromination of the β-bromo ketones to form α,β-unsaturated ketones. In order to obtain high yield of the β-bromo ketones, very mild reaction conditions would be required. Even the methods developed for operating under mild condition are still unsatisfactory because they involve the use of rather exotic starting materials such as cyclopropanols or cyclopropyl ethers which are not readily available. It would be nice to get access to the β-bromo ketones directly from easily obtainable starting materials such as α-bromo ketones.

Photoinduced C–Br bond cleavage reactions of α-bromo ketones have received much attention in mechanistic studies of organic reactions as well as in synthetic application [4]. The reaction has also been exploited in polymer chemistry as a radical initiator [5]. More recently, we have witnessed a surge of reports describing the debromination of α-bromo ketones using visible light [6]. Several years ago, we reported that UV irradiation of α-bromo valerophenone in benzene gave a mixture of β-bromo valerophenone and valerophenone in ca. 3 to 2 ratio, respectively [7] (Scheme 1).

It was suggested that the former product came from HBr addition to an initially formed α,β-unsaturated ketone, a mixture of (*E*)- and (*Z*)-1-phenylpent-2-en-1-one, which the HBr and the α,β-unsaturated ketone were formed by photoinduced C–Br homolysis followed by disproportionation of the resulting radical pairs. The reaction can be considered as a formal 1,2-Br shift reaction of α-bromo ketones. Even though photochemistry of α-bromo phenyl alkyl ketones has been extensively studied for a long time [8], only one other report except our work describing such conversion could be found in the literature up to now, in which they observed formation of β-bromoindanone as one of many products from irradiation of α-bromoindanone [9]. They explained that the β-bromoindanone came from benzylic bromination of the initially formed indanone. Since the 1,2-Br shift reaction can be very valuable in organic synthesis, we decided to investigate the reaction

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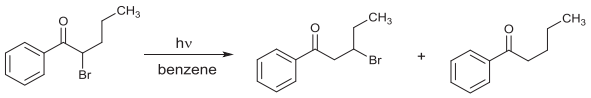
0040-4020/



Scheme 1. Photochemical reaction of α-bromovalerophenone in benzene.

more closely.

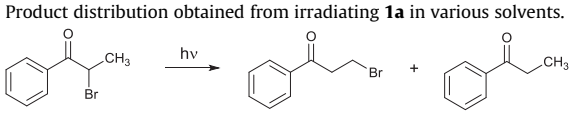
Major goals to achieve in modern organic synthesis would be to obtain high efficiency and selectivity of each reaction using eco-friendly methods. This article describes the 1,2-Br shift reaction of α-bromo ketones was explored in solution, neat and in the solid state. Because the neat and the solid state reactions are highly selective, the 1,2-Br shift fits nicely into the concept of 'atom economy' as originally coined by Trost [10]. Additional advantage of this reaction is that it can be carried out under mild conditions such as ambient temperature. Here we would like to report our results on the scope and limitation of the reaction.

2. Results and discussion

Our research started with the investigation of the photochemistry of α-bromopropiophenone, **1a**. Photolysis of the α-bromo ketone in benzene using the Pyrex filtered light of a 450 W Hanovia medium pressure mercury arc lamp gave the formal 1,2-Br shift reaction product, **2a**, as a major product with a small amount of the debrominated ketone, **3a**. Several different solvents were used to find the best solvent to obtain the best yields of **2a**, and the results are shown in Table 1.

Photolysis in other solvents also showed that **2a** was the major product, but in 2-propanol only the debrominated product, **3a**, was formed. When the photolysis was made in 9 to 1 mixture of acetonitrile and H_2O, less amount of **2a** than in pure acetonitrile was formed, in which **2a** and **3a** were formed in comparable amounts. It appears that amount of the debrominated product **3a** increases in the presence of hydrogen atom donors. It is also notable that the reaction occurs in acetone as efficiently as in other solvents, where the triplet sensitized reaction can be assumed. As shown in the above table, the reaction provided the highest yield of **2a** in acetonitrile among other solvents. Thus, acetonitrile was chosen as the solvent for photolysis studies of other ketones. The

Table 1
Product distribution obtained from irradiating **1a** in various solvents.

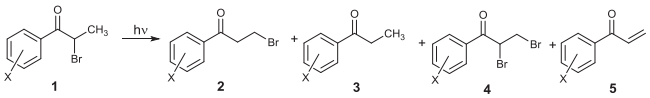


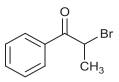
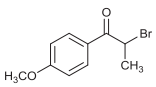
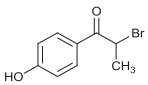
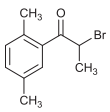
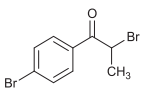
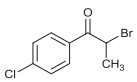
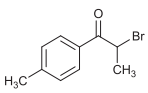
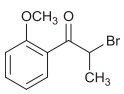
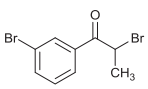
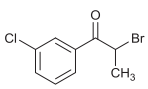
Solvent	Product distribution (%)[a]		Product selectivity (2a/3a)
	2a	3a	
acetone	76	24	3.2
acetonitrile	**96**	**4**	**24**
chloroform	95	5	19
ether	51	49	1.0
hexane	82	18	4.6
benzene	72	28	2.6
2-propanol	0	100	–
aq. acetonitrile[b]	55	45	1.2

[a] Yields were measured by integration of ^{1}H NMR signals for **1a**, **2a** and **3a** at 5.30, 3.75 and 3.01 ppm, respectively. Mass balances were 100% within experimental errors as judged by the ^{1}H NMR spectra of reaction samples which contained internal standard, methyl benzoate.

[b] 9 to 1 mixture of acetonitrile and H_2O.

Table 2
Product distribution in photolysis of α-bromopropiophenones in solution[a] and neat/solid state condition.



Compounds	Reaction condition	Product distribution (%)[b]			
		2	3	4	5
 1a	In solution	90	10	0	0
	neat	89	11	0	0
 1b	In solution	89	11	0	0
	solid	100	0	0	0
 1c	In solution	91	9	0	0
	solid	86	14	0	0
 1d	In solution	87	13	0	0
	neat	91	9	0	0
 1e	In solution[c]	44	3	9	0
	solid	100	0	0	0
 1f	In solution	90	10	0	0
	solid	100	0	0	0
 1g	In solution	94	6	0	0
	solid	100	0	0	0
 1h	In solution	89	11	0	0
	neat	100	0	0	0
 1i	In solution[c]	40	4	10	0
	neat	100	0	0	0
 1j	In solution	96	4	0	0
	neat	94	6	0	0

[a] In acetonitrile.

[b] Values obtained by integration of ^{1}H NMR signals of the starting material and the photoproducts.

[c] Secondary photoreaction products such as β-bromo propiophenone were also formed. (See the text for more information.)

results of photolysis of ring substituted α-bromo propiophenones are summarized below in Table 2.

Photolysis of α-bromopropiophenone derivatives **1a** to **1j**

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resulted in formation of product **2** as the major product in all instances. To our delight, the 1,2-Br shift reaction occurred even in neat or in the solid state in high chemical yield, even though it took much longer to complete the reaction than in solution. Photolysis in no solvent condition was performed simply by hanging a glass vial containing a small amount of liquid or solid sample by the photolysis setup. The solid state reaction times could be shortened significantly by irradiating the samples on a thin glass plate, without changing the product ratio. The most encouraging result was that product selectivity of **2** over other products increased significantly in the solid state irradiation compared to the selectivity in solution for most cases that we tried. In the case of α-bromo ketones **1b**, **1e**, **1f**, and **1g**, the corresponding β-bromo ketones **2b**, **2e**, **2f**, and **2g** are the sole solid state photoproducts observed. Thus, the solid-state photoreactions for these ketones are both selective and environmentally friendly. Only one exception to the selectivity increase in the solid state was the case of **1c** which has an OH group in the phenyl ring. We think that the OH group plays a role as a hydrogen atom donor and increases the relative amount of the photoreduction product **3** in such a condensed phase, *vide infra*.

In cases of **1e** and **1i** which have an extra Br on their phenyl rings, product analysis becomes more complicated than others because the phenyl C—Br bond cleavage can also occur. Seminal work by Wagner [11] showed that bromophenyl ketones cleaved the ring C—Br bonds very efficiently from their triplet excited states. The cleavage rate constants for *p*-bromoacetophenone and *m*-bromoacetophenone are 7×10^7 s^{-1} and 2×10^8 s^{-1}, respectively [11]. When photoreactions of **1e** and **1i** were monitored at regular time intervals, it showed that both **2** and **3** still maintaining the phenyl C—Br bond appeared first as major photoproducts and later the cleavage of the phenyl C—Br bond of primary photoproducts started to occur eventually. The result demonstrates that the cleavage of C—Br bonds at α position to carbonyls are even faster than the cleavage of C—Br bonds of phenyl rings, which means the rate constant of the former is $\gg 10^8$ s^{-1}. Scaiano and coworkers reported that the rate constant of C—Br bond cleavage of α-bromoacetophenone is above 1×10^8 s^{-1}, which is consistent with our current observation [12]. We were very excited to observe that only **2e** and **2i** were formed in photolysis of **1e** and **1i** in no solvent condition. In the solid state, both C—Br and Ph-Br bond cleavage can occur with the former being much faster rate, but the radical pairs resulting from Ph-Br bond cleavage recombine in the restricted environment while the 1,2-Br shift reaction still proceeds with no difficulty (Scheme 2).

In cases of **1f** and **1j**, which has a phenyl C—Cl bond, the C—Cl bond cleavage did not occur even at prolonged irradiation. The result is understandable by the fact that the C—Cl bond dissociation energy (84 kcal/mol) is much higher than triplet energies of phenyl alkyl ketones, which is ca. 68 kcal/mol.

When the photolysis in solution was performed without deaerating the sample, another product became a major product, which turned out to be photo-oxidation product, benzoic acid. There were a few reports describing photo-oxidation of α-bromo ketones in the presence of oxygen [13]. The amount of the photo-oxidation product was sensitive to the degree of deaerating the samples, so the deaerating procedure was essential for high yield of the 1,2-Br shift reaction.

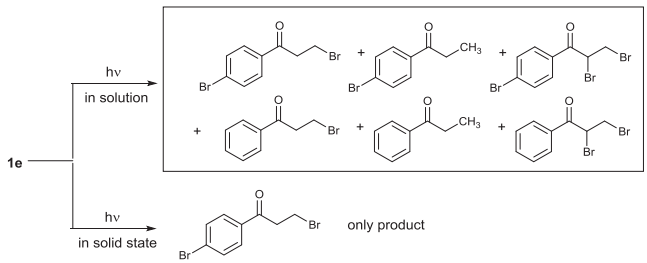
The data given in Table 2 were taken after the reaction proceeded until no starting ketones were remained. When the reaction stopped before completion, the α,β-dibrominated ketone, **4**, shown in Table 2 was also present in the product mixture in all the cases. Thus, we decided to monitor the reaction more closely by irradiating **1a** in CD_3CN at regular intervals. The result is shown in Fig. 1. At early stage of the reaction, formation of **4a** was evident together with **2a** and **3a**, but the relative amount of **4a** started to diminish and eventually disappeared as irradiation continued. It appears that photochemical reaction of **4a** is competing with that of **1a** under the given reaction condition.

We have also tested photochemistry of several other α-bromo phenyl alkyl ketones besides the above propiophenone derivatives. The results are summarized in Table 3.

For all the compounds except **1q** shown in Table 3 which have an extra alkyl/aryl group or a hetero atom at either alpha or beta position to the carbonyl group, the product selectivity of **2** over other products decreased mainly due to an increase in the amount of the elimination product **5**. As shown in Scheme 3, the elimination products **5** have structures where the alkenyl moiety can be stabilized by the extra alkyl/aryl group or the hetero atom. It seems that the stabilization of the elimination product makes addition of HBr to the enone intermediates reluctant and reduces the relative amount of **2** in product distribution. **1p** shows such an extreme example, where only **5p** was formed both in solution and solid state photolysis. Steric factors may also be important in the product distribution because putting an extra methyl group to the beta position to the carbonyl as in the case of **1k** decreases the relative amount of the 1,2-Br shift product **2k** both in solution and neat condition whereas putting it to the alpha position as in the case of **1o** does not reduce the relative amount of the 1,2-Br shift product. Interestingly **2o** was the only product in photolysis of **1o** in neat condition.

For **1k** and **1l**, the Norrish/Yang reaction [14] did not occur even though prolonged irradiation showed the Norrish/Yang reaction of primary photoproducts. Once again, the results demonstrate that the 1,2-Br shift reaction rates are extremely fast since 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].

It is worthwhile to mention that photolysis of **1n** in the solid state resulted in formation of [2 + 2] photodimer of **5n** together



Scheme 2. Product formation from photolysis of **1e** in solution and the solid-state.

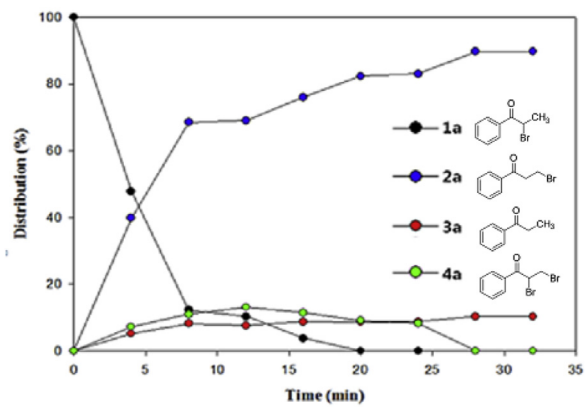


Fig. 1. Plot of product distribution vs. irradiation time in photolysis of **1a** in CD_3CN.

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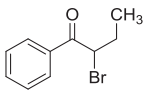
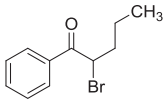
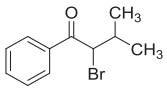
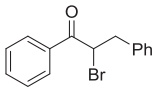
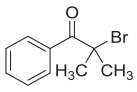
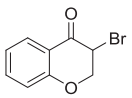
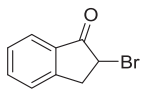
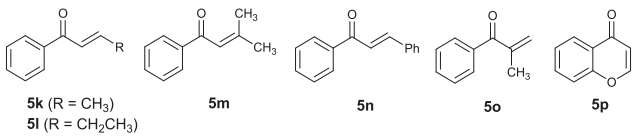
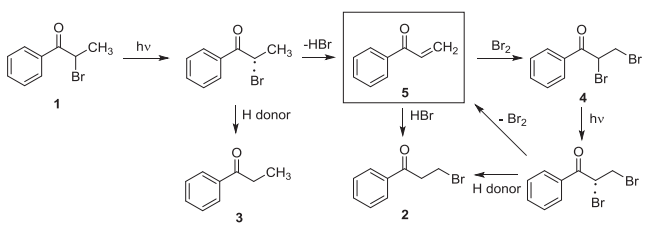
Table 3
Product distribution in photolysis of other α-bromo phenyl alkyl ketones than propiophenones in solution[a] and neat/solid state condition.

Compounds	Reaction condition	Product distribution (%)[b]			
		2	3	4	5
 1k	In solution	66	7	0	27
	neat	78	7	7	8
 1l	In solution	75	13	12	0
	neat	40	16	21	23
 1m	In solution	44	24	0	31
	solid	30	35	0	35
 1n	In solution	12	11	15	62
	solid[c]	35	22	0	0
 1o	In solution	71	0	13	16
	neat	100	0	0	0
 1p	In solution	0	0	0	100
	solid	0	0	0	100
 1q	In solution[d]	46	35	0	0
	neat	75	25	0	0

[a] In acetonitrile.
[b] Values obtained by integration of ^{1}H NMR.
[c] A [2 + 2] photodimer of **5** was also formed in 43%.
[d] Unidentified products were also formed in 19%.



Scheme 3. Structures of photoproducts **5** formed from photolysis of other α-bromo phenyl alkyl ketones than propiophenones.



Scheme 4. Proposed mechanism of photochemical reactions of α-bromopropiophenones.

with **2n** and **3n** while no such dimers were produced in solution. The chalcone skeleton of **5n** is well known to give [2 + 2] photodimers upon photolysis [16]. It seems that the dimerization pathway in the photolysis of **1n** is only competent in the solid state. Interestingly, only *trans*-head-to-head cycloaddition product was formed stereoselectively.

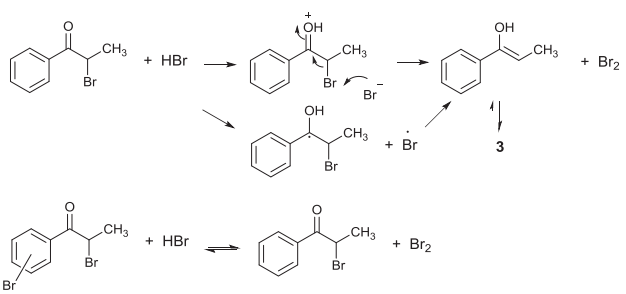
Our proposed reaction mechanism is shown in Scheme 4. We think the reaction starts from photoinduced C–Br bond cleavage of excited states of the ketones to give radical pairs since there is no reason to believe these ketones behave differently from α-bromoacetophenones whose photochemistry has been thoroughly studied mainly by Scaiano and coworkers [4].

The initially formed radical pair can either disproportionate to give the elimination product, **5**, and HBr, or abstract a hydrogen atom from any H atom donors to give the reduction product, **3**. While the rate of H atom abstraction of bromine atom to give HBr is known to be very fast [17], that of phenacyl radical may not be fast enough to compete with other paths of this reaction unless a large excess of highly active H donors are present [18]. In fact, the photoreduction is known to occur *via* rather complicated chain reaction [19], whose detailed mechanism will not be explained here except just noting that the photoreduction product can also be formed from C–Br bond cleavage of ketyl radicals that is formed by H atom abstraction of phenacyl bromides [20]. In a highly hydrogen donating solvent such as 2-propanol the reduction path predominates and **3** becomes a sole product. Along the same line, addition of a small amount of water to acetonitrile solvent was enough to produce a significant amount of the photoreduction product. It is also understandable that **1c** having *p*-hydroxy group gives non-negligible amount of reduction product while **1b** having *p*-methoxy group gives no such product in photolysis in the solid state, since the phenol moiety of **1c** can be a good source of hydrogen donors.

The fate of the elimination product **5** can be split into two events: Conjugate addition of HBr to **5** will form the 1,2-Br shift product **2**, and addition of Br_2 to **5** will give the dibrominated product **4**. The origin of Br_2 may vary depending upon reaction condition. One of them would be oxidative formation from HBr by any oxidants present in the solution such as oxygen. Even though the reaction was done in deaerated condition, a possibility of a small amount of oxygen that may still be present in the solution cannot be excluded rigorously. The other source of Br_2 would be the reaction between HBr and the starting bromo ketone, as shown in Scheme 5. The reaction may proceed by either ionic or radical mechanism. The ionic version has recently been described in the debromination of bromo ketones by bromide ion in the literature [21].

3. Conclusions

In summary, we have demonstrated that β-bromo-



Scheme 5. Origin of Br_2 in photolysis of **1**.

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propiophenones can be obtained in good yield simply by irradiating the α-bromopropiophenones in neat or solid state. The 1,2-Br shift reaction does not require volatile organic solvents and any other reagents such as acid, base or metal catalysts, etc. Besides, the method fits into perfect atom economy, which does not waste any atoms in the conversion. Thus, we have developed a synthetic method to form β-bromo arylketones in high yields, and it is environmentally friendly as it does not require any solvents.

4. Experimental section

4.1. Typical experimental procedure

All the α-bromo ketones tested for the photolysis experiment were prepared by bromination of the corresponding ketones using $CuBr_2$. The synthetic procedure has been described in our previous paper [7]. Photolysis in solution phase was done with 0.01 M solution of the ketones after purging Ar gas through the solution for a few minutes using a typical photolysis setup whose light source was the Pyrex filtered light of a 450 W Hanovia medium pressure mercury arc lamp. Photolysis in no solvent condition was done in much simpler way. A sample vial containing either liquid or sold sample was hung next to the photolysis setup and irradiated until completion. For solid samples, the reaction times could be shortened significantly by irradiating the sample doped on a thin glass plate which was simply prepared by dropping acetone solution of a given compound onto any thin glass plate and evaporating the solvent. Structural identification of photoproducts was done either by comparing them with authentic samples when they were available, or by typical spectroscopic identification procedures.

4.1.1. 2-Bromo-1-phenylpropan-1-one (**1a**) [22]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.03 (d, J = 7.7 Hz, 2H), 7.60 (t, J = 7.7 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 5.30 (q, J = 6.6 Hz, 1H), 1.91 (d, J = 6.6 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.6, 134.2, 133.9, 129.1, 129.0, 41.7, 20.4.

4.1.2. 2-Bromo-1-(4-methoxyphenyl)propan-1-one (**1b**) [23]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.02 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 5.26 (q, J = 6.6 Hz, 1H), 3.89 (s, 3H), 1.89 (d, J = 6.6 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 192.2, 164.2, 131.5, 127.1, 114.2, 55.8, 41.7, 20.5.

4.1.3. 2-Bromo-1-(4-hydroxyphenyl)propan-1-one (**1c**) [24]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.98 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 5.77 (s, 1H), 5.26 (q, J = 6.6 Hz, 1H), 1.89 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 192.3, 160.6, 131.9, 127.3, 115.8, 41.6, 20.5.

4.1.4. 2-Bromo-1-(2,5-dimethylphenyl)propan-1-one (**1d**)

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.40 (s, 1H), 7.21 (d, J = 7.7 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 5.21 (q, J = 6.6 Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 1.88 (d, J = 6.6 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 197.2, 136.3, 135.8, 135.4, 132.8, 132.1, 128.4, 45.3, 21.2, 20.7, 20.5. IR(CCl_4) 1686 cm^{-1} (C═O). HRMS ($C_{11}H_{14}^{79}BrO$, M+H) calcd. 241.0228, found 241.0232.

4.1.5. 2-Bromo-1-(4-bromophenyl)propan-1-one (**1e**) [25]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.89 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 5.22 (q, J = 6.6 Hz, 1H), 1.90 (d, J = 6.6 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 192.6, 133.0, 132.3, 130.6, 129.2, 41.4, 20.2.

4.1.6. 2-Bromo-1-(4-chlorophenyl)propan-1-one (**1f**) [26]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.97 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 5.22 (q, J = 6.6 Hz, 1H), 1.90 (d, J = 6.6 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 192.4, 140.4, 132.6, 130.6, 129.3, 41.5, 20.2.

4.1.7. 2-Bromo-1-(p-tolyl)propan-1-one (**1g**) [27]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.93 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.28 (q, J = 6.6 Hz, 1H), 2.43 (s, 3H), 1.90 (d, J = 6.6 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.2, 144.9, 131.7, 129.7, 129.3, 41.7, 22.0, 20.4.

4.1.8. 2-Bromo-1-(2-methoxyphenyl)propan-1-one (**1h**) [28]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.73 (dd, J = 7.7, 1.8 Hz, 1H), 7.51–7.44 (m, 1H), 7.05–7.01 (m, 1H), 6.97 (d, J = 8.4 Hz, 1H). 5.52 (q, J = 6.7 Hz, 1H), 3.93 (s, 3H), 1.86 (d, J = 6.7 Hz, 3H),^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 196.7, 158.2, 134.2, 131.8, 126.0, 121.2, 111.7, 56.0, 48.2, 20.5.

4.1.9. 2-Bromo-1-(3-bromophenyl)propan-1-one (**1i**) [29]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.15 (t, J = 1.8 Hz, 1H), 7.97–7.91 (m, 1H), 7.71 (ddd, J = 7.9, 1.8, 0.9 Hz, 1H), 7.37 (t, J = 7.9 Hz, 1H). 5.21 (q, J = 6.6 Hz, 1H), 1.90 (d, J = 6.6 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 192.2, 136.7, 136.0, 132.1, 130.5, 127.6, 123.3, 41.4, 20.2.

4.1.10. 2-Bromo-1-(3-chlorophenyl)propan-1-one (**1j**)

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.99 (t, J = 1.8 Hz, 1H), 7.93–7.86 (m, 1H), 7.56 (ddd, J = 8.0, 1.8, 1.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H). 5.22 (q, J = 6.6 Hz, 1H), 1.90 (d, J = 6.6 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 192.3, 135.9, 135.3, 133.8, 130.3, 129.2, 127.2, 41.5, 20.2. IR(CCl_4) 1688 cm^{-1} (C═O). HRMS ($C_9H_9^{79}BrClO$, M+H) calcd. 246.9525, found 246.9529.

4.1.11. 2-Bromo-1-phenylbutan-1-one (**1k**) [30]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.02 (d, J = 7.3 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 5.08 (t, J = 7.3 Hz, 1H), 2.30–2.20 (m, 1H), 2.19–2.09 (m, 1H), 1.09 (t, J = 7.3 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.5, 134.7, 133.9, 129.1, 129.0, 49.3, 27.1, 12.4.

4.1.12. 2-Bromo-1-phenylpentan-1-one (**1l**) [7]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.02 (d, J = 7.2 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 5.15 (dd, J = 7.8, 6.5 Hz, 1H), 2.26–2.00 (m, 2H), 1.67–1.52 (m, 1H), 1.52–1.37 (m, 1H), 0.99 (t, J = 7.4 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.5, 134.7, 133.9, 129.1, 129.0, 47.2, 35.6, 21.0, 13.8.

4.1.13. 2-Bromo-3-methyl-1-phenylbutan-1-one (**1m**)

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.00 (d, J = 7.2 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 4.94 (d, J = 8.6 Hz, 1H), 2.54–2.43 (m, 1H), 1.22 (d, J = 6.6 Hz, 3H), 1.03 (d, J = 6.6 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.9, 135.2, 133.8, 129.0, 129.0, 56.1, 31.3, 21.0, 20.7. IR(CCl_4) 1684 cm^{-1} (C═O). HRMS ($C_{11}H_{14}^{79}BrO$, M+H) calcd. 241.0228, found 241.0231.

4.1.14. 2-Bromo-1,3-diphenylpropan-1-one (**1n**) [31]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J = 8.3, 1.1 Hz, 2H), 7.55 (t, J = 6.2 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.32–7.02 (m, 6H), 5.30 (dd, J = 7.6, 7.0 Hz, 1H), 3.65 (dd, J = 14.3, 7.6 Hz, 1H), 3.34 (dd, J = 14.3, 7.0 Hz, 1H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.0, 137.7, 134.6, 134.0, 129.7, 129.1, 129.0, 128.8, 127.3, 46.8, 39.7.

4.1.15. 2-Bromo-2-methyl-1-phenylpropan-1-one (**1o**) [26]

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.14 (d, J = 8.6 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 2.04 (s, 6H),^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 197.2, 135.1, 132.6, 130.3, 128.4, 60.6, 31.8.

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*4.1.16. 2-Bromo-3,4-dihydronaphthalen-1(2H)-one (**1p**) [32]*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.94 (dd, J = 7.9, 1.5 Hz, 1H), 7.54 (t, J = 7.0 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 4.72–4.52 (m, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 185.5, 160.9, 137.0, 128.5, 122.6, 119.0, 118.2, 71.5, 45.6.

*4.1.17. 2-Bromo-2,3-dihydro-1H-inden-1-one (**1q**) [33]*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.83 (d, J = 7.5 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.44 (m, J = 11.8, 7.3 Hz, 2H), 4.65 (dd, J = 7.5, 3.1 Hz, 1H), 3.84 (dd, J = 18.1, 7.5 Hz, 1H), 3.43 (dd, J = 18.1, 3.1 Hz, 1H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 199.8, 151.3, 136.2, 133.7, 128.5, 126.6, 125.3, 44.3, 38.2.

*4.1.18. 3-Bromo-1-phenylpropan-1-one (**2a**) [34]*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.96 (d, J = 7.1 Hz, 2H), 7.60 (t, J = 6.9 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 3.75 (t, J = 6.9 Hz, 2H), 3.59 (t, J = 6.9 Hz, 2H), ^{13}C NMR (126 MHz, $CDCl_3$) δ(ppm) 197.2, 136.4, 133.8, 129.0, 128.3, 41.7, 25.9.

*4.1.19. 3-Bromo-1-(4-methoxyphenyl)propan-1-one (**2b**) [31]*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.94 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), 3.74 (t, J = 7.0 Hz, 2H), 3.52 (t, J = 7.0 Hz, 2H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.7, 164.1, 130.6, 129.6, 114.1, 55.7, 41.4, 26.4.

*4.1.20. 3-Bromo-1-(4-hydroxyphenyl)propan-1-one (**2c**) [35]*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.90 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 3.73 (t, J = 7.0 Hz, 2H), 3.52 (t, J = 7.0 Hz, 2H),^{13}C NMR (126 MHz, $CDCl_3$) δ(ppm) 196.3, 160.9, 131.0, 129.6, 115.8, 41.4, 26.2.

*4.1.21. 3-Bromo-1-(2,5-dimethylphenyl)propan-1-one (**2d**)*

^{1}H NMR (500 MHz,$CDCl_3$) δ (ppm) 7.44 (s, 1H), 7.21 (d, J = 7.7 Hz, 1H), 7.15 (d, J = 7.7 Hz, 1H), 3.72 (t, J = 6.8 Hz, 2H), 3.50 (t, J = 6.8 Hz, 2H), 2.47 (s, 3H), 2.37 (s, 3H),^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 200.9, 137.0, 135.7, 135.5, 132.8, 132.3, 129.4, 44.2, 26.4, 21.2, 21.1. IR(CCl_4) 1683 cm^{-1} (C═O). HRMS ($C_{11}H_{14}^{79}BrO$, M+H) calcd. 241.0228, found 241.0234.

*4.1.22. 3-Bromo-1-(4-bromophenyl)propan-1-one (**2e**) [34]*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.82 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 3.73 (t, J = 6.8 Hz, 2H), 3.54 (t, J = 6.8 Hz, 2H),^{13}C NMR (126 MHz, $CDCl_3$) δ(ppm) 196.2, 135.2, 132.3, 129.8, 129.1, 41.7, 25.6.

*4.1.23. 3-Bromo-1-(4-chlorophenyl)propan-1-one (**2f**) [36]*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.90 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 3.73 (t, J = 6.8 Hz, 2H), 3.55 (t, J = 6.8 Hz, 2H),^{13}C NMR (126 MHz, $CDCl_3$) δ(ppm) 196.0, 140.3, 134.8, 129.7, 129.3, 41.7, 25.7.

*4.1.24. 3-Bromo-1-(p-tolyl)propan-1-one (**2g**) [34]*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.86 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 3.74 (t, J = 7.0 Hz, 2H), 3.55 (t, J = 7.0 Hz, 2H), 2.42 (s, 3H),^{13}C NMR (126 MHz, $CDCl_3$) δ(ppm) 196.8, 144.7, 134.0, 129.6, 128.4, 41.6, 26.2, 21.9.

*4.1.25. 3-Bromo-1-(2-methoxyphenyl)propan-1-one (**2h**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.77 (dd, J = 7.7, 1.8 Hz, 1H), 7.49 (t, J = 6.9 Hz, 1H), 7.02 (t, J = 7.1 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 3.93 (s, 3H), 3.71 (t, J = 6.9 Hz, 2H), 3.60 (t, J = 6.9 Hz, 2H),^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 198.9, 159.1, 134.4, 130.8, 127.3, 121.0, 111.8, 55.7, 47.0, 26.7. IR(CCl_4) 1669 cm^{-1} (C═O). HRMS ($C_{10}H_{12}^{79}BrO_2$, M+H) calcd. 243.0021, found 243.0026.

*4.1.26. 3-Bromo-1-(3-bromophenyl)propan-1-one (**2i**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.08 (s, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.37 (t, J = 7.9 Hz, 1H), 3.73 (t, J = 6.8 Hz, 2H), 3.55 (t, J = 6.8 Hz, 2H), ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 195.9, 136.7, 131.4, 130.6, 129.0, 126.8, 123.4, 41.8, 25.5. IR(CCl_4) 1690 cm^{-1} (C═O). HRMS ($C_9H_9^{79}Br_2O$, M+H) calcd. 290.9020, found 290.9027.

*4.1.27. 3-Bromo-1-(3-chlorophenyl)propan-1-one (**2j**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.92 (s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 7.9 Hz, 1H), 3.73 (t, J = 6.8 Hz, 2H), 3.55 (t, J = 6.8 Hz, 2H),^{13}C NMR (126 MHz, $CDCl_3$) δ(ppm) 195.9, 137.9, 135.4, 133.7, 130.3, 128.4, 126.3, 41.8, 25.5. IR(CCl_4) 1691 cm^{-1} (C═O). HRMS ($C_9H_9^{79}BrClO$, M+H) calcd. 246.9525, found 246.9519.

*4.1.28. 3-Bromo-1-phenylbutan-1-one (**2k**) [37]*

^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm) 7.96 (d, J = 7.1 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 4.75–4.67 (m, 1H), 3.73 (dd, J = 17.3, 6.9 Hz, 1H), 3.40 (dd, J = 17.3, 6.7 Hz, 1H), 1.82 (d, J = 6.7 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 136.6, 133.7, 129.0, 128.3, 49.6, 43.6, 26.7.

*4.1.29. 3-Bromo-1-phenylpentan-1-one (**2l**) [7]*

^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.97 (d, 2H, J = 7.5 Hz), 7.53 (m, 3H), 4.58 (m, 1H), 3.74, 3.42 (doublets of AB quartets, 2H, J = 17.2, 7.2 Hz), 1.97 (m, 2H), 1.11 (t, 3H, J = 7.2 Hz), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 196.9, 136.7, 133.5, 128.8, 128.2, 51.8, 47.4, 32.2, 12.2.

*4.1.30. 3-Bromo-2-methyl-1-phenylpropan-1-one (**2o**) [38]*

^{1}H NMR (500 MHz,$CDCl_3$) δ (ppm) 7.96 (d, J = 7.1 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 3.95–3.87 (m, 1H), 3.80 (dd, J = 9.9, 7.0 Hz, 1H), 3.44 (dd, J = 9.9, 6.4 Hz, 1H), 1.33 (d, J = 7.0 Hz, 3H), ^{13}C NMR (126 MHz, $CDCl_3$) δ(ppm) 201.5, 136.0, 133.7, 129.0, 128.6, 43.8, 34.1, 17.9.

*4.1.31. 4H-Chromen-4-one (**5p**) [39]*

^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm) 8.26 (dd, J = 8.0, 1.5 Hz, 1H), 7.99 (d, J = 5.9 Hz, 1H), 7.75 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 6.68 (d, J = 5.8 Hz, 1H),^{13}C NMR (126 MHz, $CDCl_3$) δ(ppm) 177.9, 156.7, 155.5, 134.0, 126.0, 125.5, 125.1, 118.4, 113.2.

Conflicts of interest

There are no conflicts to declare.

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