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Microwave-assisted synthesis of α-hydroxy ketone and α-diketone and pyrazine derivatives from α-halo and α,α′-dibromo ketone

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Abstract—A novel reaction of α-halo ketone (α-bromo and α-chloro ketone) with irradiation under microwave gave the corresponding α-hydroxyketone and pyrazine derivative in good yields. In the case of α,α′-dibromo ketone, α-diketone was obtained. This reaction affords a new, clean and convenient synthetic method for α-hydroxyketone, α-diketone, α-chloro ketone and pyrazine derivative.

In the synthesis of various natural products and pharmacologically active compounds, α-hydroxycarbonyl compounds are potentially valuable synthetic intermediates for the preparation of a range of compounds of biological products such as substituted 2-amino-1-arylethanols.[1]

α-Hydroxyketones are usually prepared by one of the following methods: α-hydroxylation by treatment of their enolate forms with a molybdenum peroxide reagent in THF–hexane at −70 °C,[2] transformation of the enamine derivatives of ketones to α-hydroxy derivatives by molecular oxygen,[3] and α-hydroxylation of silyl enol ethers with *m*-chloroperbenzoic acid,[4] or with certain other oxidizing agents.[5]

It is known that there has been considerable interest in the development of direct methods for the synthesis of α-hydroxyketones using nontoxic hypervalent iodine reagents, which involve the following methods: reaction of ketone with iodobenzene diacetate in the presence of potassium hydroxide in methanol and then hydrolysis of the dimethylacetals;[6] oxidation of enol silyl ether of acetophenone using the system iodosobenzene/boron trifluoride etherate/water in methylene chloride at −40 °C;[7] and reaction of ketones with [bis(trifluoroacetoxy)] iodobenzene and trifluoroacetic acid in acetonitrile–water under acidic conditions.[8]

During the course of our studies, α-iodo cycloalkanones are important as intermediates in organic synthesis, which were synthesized in our laboratory by a new method.[9] These iodo ketones are unstable and sensitive to light. We thus tried to obtain useful products from these iodo compounds. In this series, we have already shown that the photo-dehydroiodination from α-iodocycloalkanones in hexane affords α,β-unsaturated ketones as major products, accompanied by photoreduced products as by-products. In hexane containing a small amount of water, the substituted product 2-hydroxycycloalkanone was also obtained.[10] In our previous letter, we found that the reaction of α-iodoketone with irradiation under a high-pressure mercury lamp gave the corresponding α-hydroxyketone in good yields.[11] However, these methods suffer some drawbacks. The most serious of these is the use of organic solvents and ammonium cerium(IV) nitrate for the synthesis of α-iodoketone.

The use of microwaves in organic synthesis has attracted considerable attention in recent years. It is known that microwaves shorten the time, enhance reaction rates, and improve product yields.[12] So, we tried the reaction of α-bromo ketone in water under irradiation with microwaves to overcome this problem. Herein, we report that the irradiation of α-bromo- **1**–**11**, and α-chloro alkanones **1′**–**10′** in water gave α-hydroxyketones **1a**–**11a**.

The irradiation of α-bromo- **1**–**11** and α-chloro alkanones **1′**–**10′** in water at 100–160 °C under microwave

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irradiation for 15 to 20 min gave the corresponding α-hydroxyketones **1a**–**11a** in good yields. These results are summarized in Table 1.

As can be seen from Table 1, it was found that the reaction gives preferentially α-hydroxyketone. Thus, in order to discuss the reactivity of α-bromo cyclicketone, it was compared with that of the chloro derivatives. From these results, both α-bromo- and α-chloro ketone showed similar reactivities. The use of microwaves was found to significantly improve the reaction yields and shorten the reaction time in comparison with heat conditions (Schemes 1 and 2). In the case of α-bromo acyclic ketones **12** and **13**, the corresponding 3-hydroxy- **12a** and 4-hydroxy ketone **13a** were obtained in 82% and 75% yields, respectively (Scheme 3).

In order to substitute the bromide into the chloride ion, we attempted the reaction of α-bromo ketone under microwave irradiation with NaCl solution. The reaction of α-bromo ketones **2**, **3**, **4**, **6**, **7**, **8**, and **11** in 3% NaCl solution gave the corresponding α-chloro ketone in good yields. These results are summarized in Table 2. As can be seen from Table 2, it was found that the reaction gives preferentially α-chloro ketone by the conventional method (Table 2).

We further developed the generality of the substituted reaction into amino group in ammonia water. The reaction of **2** in 7% ammonia water under microwave irradiation gave tricyclic pyrazine **2e**[13] in a good yield and in the case of some α-halo ketones (**1′**, **2″**, **5**, **8** and **12**), the corresponding pyrazine derivatives in a

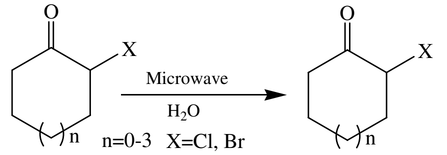
Table 1. Reaction of α-halo ketone in water under microwave or heat

Run	Substrate	*n*	R^1	R^2	R^3	Reaction type	Temperature (°C)	Time (min)	Product (%)	
1	**1**	0				MW	100	25	**1a**	88[a] (47)[b]
2	**1**	0				Heat	100	25	**1a**	6 (2)
3	**2**	1				MW	125	15	**2a**	100 (62)
4	**2**	1				Heat	125	15	**2a**	2 (0)
5	**3**	2				MW	150	25	**3a**	86 (80)
6	**3**	2				Heat	150	25	**3a**	3 (0)
7	**4**	3				MW	160	25	**4a**	84 (66)
8	**4**	3				Heat	160	25	**4a**	3 (2)
9	**1′**	0				MW	100	25	**1a**	92 (49)
10	**1′**	0				Heat	100	25	**1a**	3 (1)
11	**2′**	1				MW	125	15	**2a**	98 (71)
12	**2′**	1				Heat	125	15	**2a**	0 (0)
13	**3′**	2				MW	150	25	**3a**	88 (79)
14	**3′**	2				Heat	150	25	**3a**	2 (1)
15	**4′**	3				MW	160	25	**4a**	85 (70)
16	**4′**	3				Heat	160	25	**4a**	2 (2)
17	**5**		H	H	H	MW	125	25	**5a**	89 (88)
18	**5**		H	H	H	Heat	125	25	**5a**	59 (41)
19	**6**		Me	H	H	MW	125	25	**6a**	91 (76)
20	**6**		Me	H	H	Heat	125	25	**6a**	42 (33)
21	**7**		H	Me	H	MW	125	25	**7a**	90 (80)
22	**7**		H	Me	H	Heat	125	25	**7a**	54 (47)
23	**8**		H	H	Me	MW	125	25	**8a**	84 (74)
24	**8**		H	H	Me	Heat	125	25	**8a**	27 (21)
25	**9**		H	H	Cl	MW	100	25	**9a**	99 (90)
26	**9**		H	H	Cl	Heat	100	25	**9a**	38 (31)
27	**10**		H	H	Br	MW	125	25	**10a**	96 (82)
28	**10**		H	H	Br	Heat	125	25	**10a**	20 (12)
29	**11**		H	H	OMe	MW	125	25	**11a**	99 (81)
30	**11**		H	H	OMe	Heat	125	25	**11a**	21 (18)
31	**5′**		H	H	H	MW	125	25	**5a**	93 (88)
32	**5′**		H	H	H	Heat	125	25	**5a**	0 (0)
33	**6′**		Me	H	H	MW	125	25	**6a**	94 (78)
34	**6′**		Me	H	H	Heat	125	25	**6a**	0 (0)
35	**7′**		H	Me	H	MW	125	25	**7a**	93 (85)
36	**7′**		H	Me	H	Heat	125	25	**7a**	0 (0)
37	**8′**		H	H	Me	MW	125	25	**8a**	86 (83)
38	**8′**		H	H	Me	Heat	125	25	**8a**	0 (0)
39	**9′**		H	H	Cl	MW	100	25	**9a**	99 (88)
40	**9′**		H	H	Cl	Heat	100	25	**9a**	0 (0)
41	**10′**		H	H	Br	MW	125	25	**10a**	91 (82)
42	**10′**		H	H	Br	Heat	125	25	**10a**	0 (0)

Reaction conditions: Substrate (0.05 mmol) in water (3 ml) was irradiated by MW power (200 W).

[a] Yields were determined by GLC.

[b] Isolated yields.

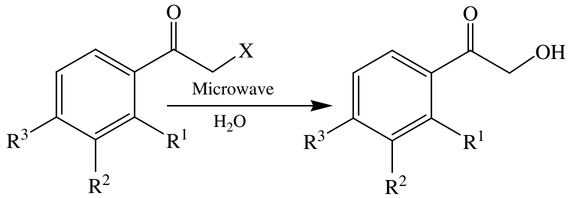


1: n=0, X=Br
2: n=1, X=Br
3: n=2, X=Br
4: n=3, X=Br
1': n=0, X=Cl
2': n=1, X=Cl
3': n=2, X=Cl
4': n=3, X=Cl

1a: n=0, X=OH
2a: n=1, X=OH
3a: n=2, X=OH
4a: n=3, X=OH

Scheme 1.

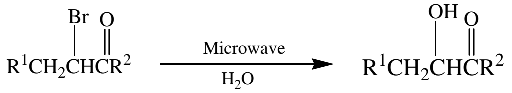
good yield. In the case of **4**, 2-aminocyclooctanone (**4f**) and, not the pyrazine derivative was obtained. These results are summarized in Tables 3 and 4. From these results, it is considered that α-bromo ketones are easily converted to pyrazines via the self-condensation of initially formed α-aminoketones. It seems that in the case of 2-aminocyclooctanone (**4f**), the condensation did not occur due to the flexibility of an 8-membered ring. As can be seen in Tables 3 and 4, it was found that the reaction yields the corresponding pyrazine derivatives by a simple and conventional method.



5: X=Br, R^1=R^2=R^3=H
5': X=Cl, R^1=R^2=R^3=H
6: X=Br, R^1=Me, R^2=R^3=H
6': X=Cl, R^1=Me, R^2=R^3=H
7: X=Br, R^1=R^3=H, R^2=Me
7': X=Cl, R^1=R^3=H, R^2=Me
8: X=Br, R^1=R^2=H, R^3=Me
8': X=Cl, R^1=R^2=H, R^3=Me
9: X=Br, R^1=R^2=H, R^3=Cl
9': X=Cl, R^1=R^2=H, R^3=Cl
10: X=Br, R^1=R^2=H, R^3=Br
10': X=Cl, R^1=R^2=H, R^3=Br
11: X=Br, R^1=R^2=H, R^3=OMe

5a: R^1=R^2=R^3=H
6a: R^1=Me, R^2=R^3=H
7a: R^1=R^3=H, R^2=Me
8a: R^1=R^2=H, R^3=Me
9a: R^1=R^2=H, R^3=Cl
10a: R^1=R^2=H, R^3=Br
11a: R^1=R^2=H, R^3=OMe

Scheme 2.

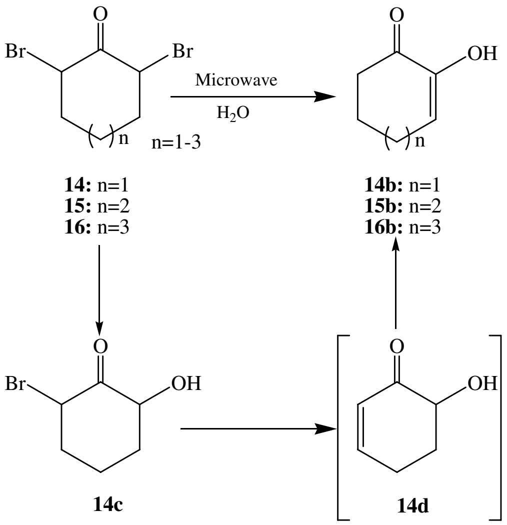


$$R^1CH_2CH(Br)C(=O)R^2 \xrightarrow[H_2O]{Microwave} R^1CH_2CH(OH)C(=O)R^2$$

12: R^1=Me, R^2=Pr
13: R^1=Et, Bn^n

12a: R^1=Me, R^2=Pr Yield: 82%
13a: R^1=Et, Bn^n Yield: 75%

Scheme 3.



Scheme 4.

Moreover, it is interesting that in the case of α,α′-dibromo cyclicketones, α-diketones were obtained in good yields. The reaction of α,α′-dibromo ketones **14**–**16** in water gave the corresponding α-diketones **14b**–**16b** in a good yield. These results are summarized in Table 5.

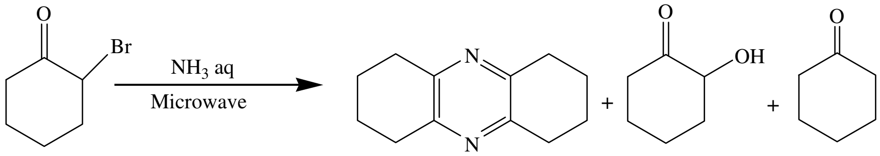
It was found that, in view of green chemistry, this synthetic method affords a new, clean and convenient method for α-diketones (Scheme 4).

Table 2. Microwave reaction of α-bromo ketone in 3% NaCl solution

Run	Substrate		Temperature (°C)	Time (min)	Hydroxy ketone	Product (%)[a]	
						Diketone	Chloro ketone
1	**2**	None	75	15	14	0	0
2	**2**	NaCl	75	15	5	1	43
3	**2**	NaCl	100	15	25		75
4	**3**	NaCl	115	50	25		74
5	**4**	NaCl	115	100	80		19
6	**6**	NaCl	80	120			93
7	**7**	NaCl	100	50			85
8	**8**	None	75	25	61	3	0
9	**8**	NaCl	75	25	1	1	48
10	**8**	NaCl	80	120			73
11	**11**	NaCl	75	50			91

Reaction conditions: Substrate (0.05 mmol) in NaCl solution (3 ml) and MW power (40 W) were employed.
[a] Yields were determined by GLC.

Table 3. Microwave reaction of α-bromo ketone **2** in 7% NH_3 solution



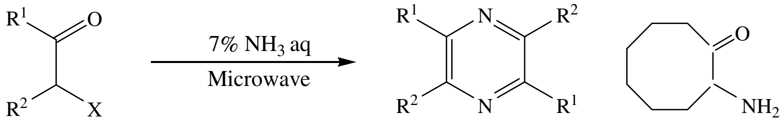
2 **2e** **2a** **2c**

Run	Temperature (°C)	Time (min)	Product (%)[a]		
			2e	**2a**	**2c**
1	30	10	6	24	—
2	50	10	65	13	3
3	70	10	92	—	7
4	90	10	93	—	4
5	105	10	95	—	2
6	125	10	98	—	1

Reaction condition: Substrate (0.05 mmol) in 7% NH_3 solution (5 ml), and the apparatus (DISCOVER, CEM Corporation) using microwave power (150 W) were employed.

[a] Yields were determined by GLC.

Table 4. Microwave reaction of α-bromo and α-chloro ketone in 7% NH_3 solution



X=Br,Cl **e** **4f**

Run	R^1	R^2	X	Substrate	Product (%)[a]
1	$–CH_2CH_2CH_2–$		Cl	**1′**	**1e** (88)
2	$–CH_2CH_2CH_2–$		Br	**2**	**2e** (95)
3	$–CH_2CH_2CH_2CH_2–$		Cl	**2′**	**2e** (90)
4	$–CH_2CH(CH_3)CH_2CH_2–$		Br	**2″**	**2″e** (83)
5	$–CH_2(CH_2)_4CH_2–$		Br	**4**	**4f** (70)
6	Ph	H	Br	**5**	**5e** (74)
7	*p*-MePh	H	Br	**8**	**8e** (74)
8	*p*-MeOPh	H	Br	**11**	**11e** (71)
9	$C_3H_7–$	$C_2H_5–$	Br	**12**	**12e** (50)

Reaction condition: Substrate (0.05 mmol) in 7% NH_3 solution (5 ml) at 105 °C for 10 min was irradiated by microwave.

[a] Yields were determined by GLC.

Table 5. Reaction of α,α′-dibromo ketone in water under microwave or heat[a]

Run	Substrate	Reaction Type	Temperature (°C)	Time (min)	Product (%)[b]
1	**14**	MW	125	15	**14b** (87)
2	**14**	Heat	125	15	**14b** (3)
3	**15**	MW	150	25	**15b** (87)
4	**15**	Heat	150	25	**15b** (10)
5	**16**	MW	150	25	**16b** (60)
6	**16**	Heat	150	25	**16b** (10)

[a] Reaction conditions: Substrate (0.05 mmol) in water (3 ml) was irradiated by microwave.

[b] Yields were determined by GLC.

In order to investigate the reaction pathway of the α-diketone for α,α′-dibromocyclohexanone (**14**), the microwave irradiation of **14** was carried out. The reaction of **14** at 75 °C gave α-diketone **14b** (39%) and 2-bromo-6-hydroxycyclohexanone (**14c**) (61%) as unstable intermediates. Moreover, it was found that the reaction mixtures were converted into α-diketone under irradiation at 125 °C. From these results, it is considered that this reaction first proceeds to substitute halogen for a hydroxyl group, followed by dehydrobromination occurs, and then double bond produced was isomerized.

In Table 6, the microwave apparatus (DISCOVER, CEM Corporation) was compared with that of the unmodified domestic microwave oven NE-S330F (National). It was found that the reaction using the former apparatus gives higher yields and in a shorter reaction time than the latter.

In conclusion, we have developed a very clean, simple and convenient method for the synthesis of α-hydroxyketones and α-diketones. It is particularly noteworthy that this reaction affords a new synthetic method for α-hydroxyketones and α-diketones. Moreover, it is interesting that we have succeeded in establishing a

Table 6. Effects of two equipments for α-hydroxylation of α-bromo ketone

Run	Substrate	Equipment	Power (W)	Time (min)	Product (%)[c]
1	**2**	Commercial microwave[a]	170	10	**2a** (17)
2	**2**	Commercial microwave[a]	700	10	**2a** (28)
3	**2**	DISCOVER (CEM)[b]	200	10	**2a** (62)
4	**8**	Commercial microwave[a]	170	43	**8a** (33)
5	**8**	Commercial microwave[a]	700	50	**8a** (65)
6	**8**	DISCOVER (CEM)[b]	200	10	**8a** (74)

[a] Reaction conditions: Substrate (0.05 mmol) in water (3 ml) was irradiated by micro wave. Commercial microwave equipments were used by NE-S330F (National).

[b] Reaction conditions: Substrate (0.05 mmol) in water (3 ml) and pressure (15 bar) at 125 °C were employed.

[c] Isolated yields.

convenient synthesis of α-chloro ketone and pyrazine derivatives, which is more convenient than the method used heretofore. The use of microwaves was found to significantly improve the reaction yields and shorten the reaction time of the key step reactions.

1. Typical procedure 1: irradiation of 2-bromo cyclooctanone (4) by microwaves in water

A mixture of α-bromo ketone (0.14 mmol) and water (3 ml) was irradiated (120W) using a microwave generating equipment (DISCOVER®, CEM Corporation) at 120 °C for 25 min. After the irradiation was completed, the mixture was extracted with diethyl ether (30 ml). The ethereal solution was washed with a saturated solution of sodium thiosulfate (2 × 2.0 ml), saturated aq NaCl (2 × 2.0 ml) and water (2 × 2.0 ml). The ethereal solution was dried over Na_2SO_4 and concentrated in a vacuum. The resulting oil was chromatographed on silica gel. Elution with hexane–ether (3:1) gave 2-hydroxycyclooctanone (**4a**) as a pale-yellow oil (14 mg, 70%).

1.1. 2-Hydroxycyclooctanone (4a)[11b,c]

Pale-yellow oil; IR (NaCl) 3475 and 1701 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 4.19$ (dd, 1H, $J = 1.9$, 4.3 Hz, C*H*OH), 3.79 (br s, 1H, CHO*H*), 2.71 (dt, 1H, $J = 2.6$, 8.5 Hz, C(O)C*H*H), 2.30–2.45 (m, 2H), 1.91–2.08 (m, 2H), 1.62–1.87 (m, 4H), 1.32–1.45 (m, 2H) and 0.85–0.97 (m, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 217.6$, 76.1, 37.4, 29.2, 28.3, 25.7, 24.8 and 22.1; MS (EI) *m*/*z* 142 (M^+), 124 ($[M-H_2O]^+$), 113, 98, 81, 57, and 41; MS (CI) *m*/*z* 143 ($[M+1]^+$).

2. Typical procedure 2: irradiation of 2-bromo cyclohexanone (2) by microwave in a 7% NH_3 water

A mixture of α-bromo ketone (0.266 mmol) and 7% NH_3 water (5 ml) was irradiated (150 W) using a microwave generating equipment (DISCOVER®, CEM Corporation) at 120 °C for 20 min. After the irradiation was completed, the mixture was extracted with diethyl ether (30 ml). The ethereal solution was washed with a saturated solution of sodium thiosulfate (2 × 2.0 ml), saturated aq NaCl (2 × 2.0 ml) and water (2 × 2.0 ml). The ethereal solution was dried over Na_2SO_4 and concentrated in a vacuum. The resulting oil was chromatographed on silica gel. Elution with hexane–ether (3:1) gave 1,2,3,4,5,6,7,8-octahydrophenazine (**2e**) as a white crystal (22 mg, 86%).

2.1. 1,2,3,4,5,6,7,8-octahydrophenazine(2e)[13a–e]

Mp 105–107 °C; IR (KBr) 1433, 1394, 1334, 1192, 1130, 982, 872, and 816 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.4$–2.2 (br, 8H) and 2.4–3.1 (br, 8H), ^{13}C NMR ($CDCl_3$) $\delta = 149.3$, 31.6, and 22.8; MS (EI) *m*/*z* 188 (M^+), 173, 160, 145, 132, 120, 94, 79, 77, and 65.

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