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Facile one-pot synthesis of α-bromoketones from olefins using bromide/bromate couple as a nonhazardous brominating agent

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ABSTRACT

A new method for the preparation of α-bromoketones from olefins using bromide/bromate couple as a nonhazardous brominating agent has been developed. Several α-bromoketones were successfully prepared from a variety of olefins by this method. This procedure is an alternative to conventional molecular bromine.

α-Bromoketones are versatile intermediates in organic synthesis.[1] Numerous methods have been developed for the preparation of α-bromoketones from ketones with liquid bromine in the presence of protic and Lewis acids.[2] Bromine is hazardous with associated risks in handling and transport. However, it is still being used by industry as well as academia due to its easy availability, low cost, and lack of a better alternative. A few other alternative procedures for α-bromination of carbonyl compounds avoiding liquid bromine involve *N*-bromosuccinimide (NBS)[3] and 4,4-dibromo-2,6-di-*tert*-butyl-cyclohexa-2,5-dienone.[4] Nevertheless, these brominating reagents have some limitations including their low atom efficiency and use of molecular bromine for their preparation.

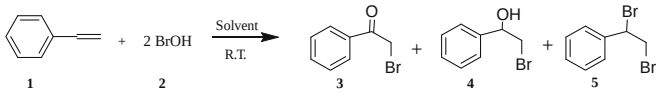
A survey of the existing literature revealed that α-bromoketones have been synthesized mainly from ketones.[2–4] Surprisingly, we have found limited reports for the preparation of α-bromoketones from olefins.[5] The direct conversion of alkenes to α-chloroketones is reported with chromyl chloride.[6] However, the same strategy for α-bromoketones is not explored in the literature.

Despite the fact that, the reactions of olefins with NBS is well documented in the literature to obtain bromohydrins,[7] it is seldom extended to get α-bromoketones. As olefins substituted with a variety of functionalities are easily accessible we assumed that a convenient procedure from olefins using an alternative mild brominating agent will be appreciated.

Our continuous efforts to achieve maximum bromide atom efficiency and minimize waste generation, as well as elimination of the use of hazardous liquid bromine led us to develop a versatile brominating reagent, a bromide–bromate couple, and we have already demonstrated a few useful applications.[8]

Herein, we report further results using this brominating reagent for the direct synthesis of α-bromoketones from olefins

Table 1
Optimization of reaction conditions for α-bromoketone synthesis



1 2 3 4 5

Entry	Solvent	Time (h)	Product ratio[a]		
			3	**4**	**5**
1	Dioxane	8	71	17	12
2	Acetonitrile	8	40	47	8
3	THF	8	3	39	24
4	CH_2Cl_2	8	–	19	77
5	Et_2O	8	13	3	76
6	DMSO	8	–	60	8
7[b]	Dioxane	7.5	60	11	1
8[c]	Dioxane	7.5	61	10	2
9[d]	Dioxane	8	36	52	3

[a] GC yields unless otherwise stated.
[b] Isolated yield with 2.5 equiv of BrOH.
[c] Isolated yield with 3.0 equiv of BrOH.
[d] Reaction with NBS.

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Table 2
Synthesis of various α-bromoketones from olefins

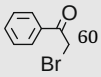
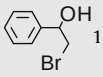
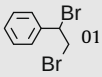
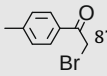
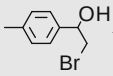
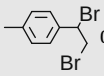
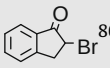
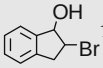
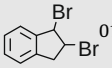
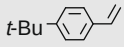
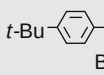
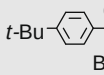
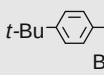
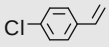
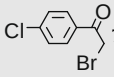
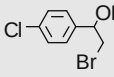
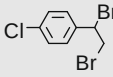
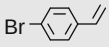
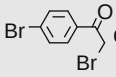
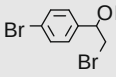
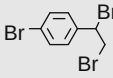
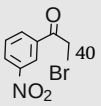
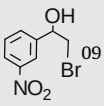
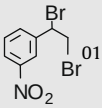
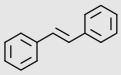
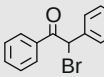
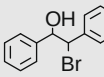
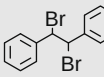
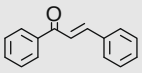
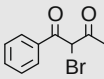
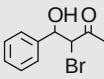
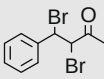
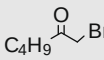
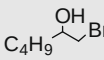
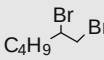
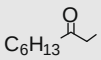
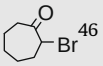
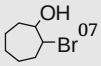
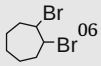
Entry	Substrate	Time (h)	Isolated yields (%)			Ref.
			Bromoketone	Bromohydrin	Dibromo	
1		7.5	 60	 12	 01	10
2		6	 87	 11	 02	10
3		6	 86	 10	 01	2i
4		6	 82	 11	 02	
5		6.5	 77	 12	 02	11
6		6.5	 68	 25	 03	11
7		15	 40	 09	 01	2e
8		7	 77	 15	 02	10
9		10	 64	 10	 03	8a
10	C_4H_9	8	 Br 50	 Br17	 Br07	
11	C_6H_{13}	7	 Br 68	Br20	Br04	
12	C_7H_{15}	13	Br 64	Br08	Br03	10
13	C_8H_{17}	13	Br 70	Br07	Br03	
14	C_9H_{19}	7.5	Br 70	Br07	Br03	
15	$C_{10}H_{21}$	14	Br 82	Br06	Br02	
16	$C_{12}H_{25}$	15	Br 65	Br08	Br03	

Table 2 (*continued*)

Entry	Substrate	Time (h)	Isolated yields (%)			Ref.
			Bromoketone	Bromohydrin	Dibromo	
17	$C_{14}H_{29}$—═	14	$C_{14}H_{29}$ O Br 67	$C_{14}H_{29}$ OH Br09	$C_{14}H_{29}$ Br Br03	
18	$C_{16}H_{33}$—═	14	$C_{16}H_{33}$ O Br 65	$C_{16}H_{33}$ OH Br08	$C_{16}H_{33}$ Br Br03	
19		8	 46	 07	 06	8b
20		9	 46	 07	 06	8b

under ambient conditions. In our earlier communication,[8a] we showed the generation of active species BrOH by reacting bromide–bromate and acid in the ratio of 2:1:3, respectively (Eq. 1):

$$2Br^- + BrO_3^- + 3H^+ \rightarrow 3BrOH \quad (1)$$

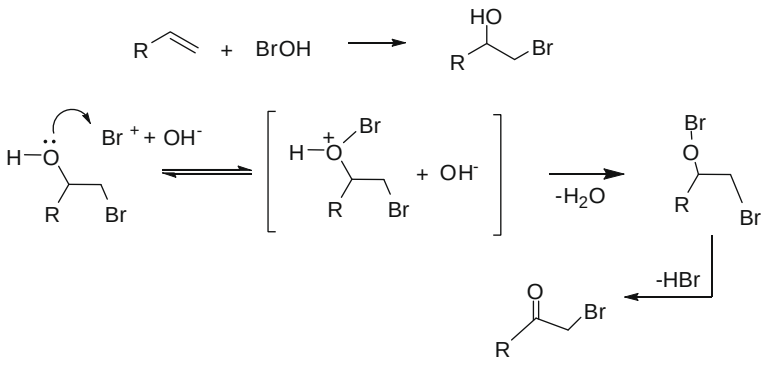
The reaction of BrOH with olefins to provide α-bromoketones is investigated. To optimize the reaction conditions we initiated our studies with styrene **1** as a representative olefin in different solvents at room temperature. When the reaction was carried out with 1,4-dioxane as solvent with 2.0 equiv of brominating reagent, the products α-bromoacetophenone **3**, 2-bromo-1-phenylethanol **4,** and styrene dibromide **5** were obtained in 71%, 17%, and 12% yields, respectively (GC) (Table 1, entry 1). When the reaction was performed in acetonitrile, the yield of product **3** was reduced to 40% (entry 2), bromohydrin **4** being the major product in 47% along with 8% of product **5**. Whereas THF, dichloromethane, and diethyl ether provided desired product **3** in 3%, 0%, and 13% yields, respectively, and products **4** and **5** are obtained as major ones. When the reaction was conducted in dimethylsulfoxide (DMSO) at room temperature, the reaction does not yield bromoketone; however, it gave bromohydrin (**4**) as the major product (60% isolated yield) and dibromo derivative (**5**) in 8% yield and the rest constituted unidentified bromo impurities (entry 6). To optimize the amount of the reagent **2**, we performed two reactions in dioxane employing 2.5 and 3.0 equiv of reagent **2.** The gradual increase of the reagent from 2 to 2.5 and 3 equiv gave the desired product (**3**) in 60% and 61% isolated yields, respectively (entries 7 and 8). The results clearly indicate that the best yield of the desired product could be obtained in dioxane with 2.1 equiv of reagent BrOH. Therefore the following experiments were performed under these optimized conditions in dioxane, unless otherwise required.[9]

When we carried out the reaction of styrene with *N*-bromosuccinimide[7] (2.1 equiv) under identical conditions the desired product (**3**) was obtained only in 36% yield (Table 1, entry 9). This study further supports the significance of the present reagent for obtaining α-bromoketones directly from olefins in good yields.

Several alkenes were subjected to this procedure to produce the corresponding α-bromoketones (Table 2). 4-Methyl styrene and indene (Table 2, entries 2 and 3.) showed high selectivity to provide 4-methyl-α-bromoacetophenone and 2-bromo-indan-1-one in 87% and 86% isolated yields. These transformations are associated with undesired products during bromination using HBr/H_2O_2.[10] When this methodology was applied to 3-nitro styrene (Table 2, entry 7) the corresponding 3-nitro-α-bromoacetophenone was obtained in 40% yield. Such deactivated substrates are reported to be tedious by other methods.[3a] The internal olefins stilbene and chalcone were smoothly converted to 2-bromo-1,2-diphenyl-ethanone and 2-bromo-1,3-diphenylpropane-1,3-dione, respectively, in good yields (Table 2, entries 8 and 9). Under the same experimental conditions straight chain as well as cyclic olefins underwent brominations without any difficulty to provide the corresponding α-bromoketones in moderate to good yields (Table 2, entries 10–20).

As indicated in Eq. 1, the active species BrOH reacts with olefins to provide bromohydrin[8a] which further reacts with another equivalent of BrOH to give the corresponding α-bromoketones as outlined in Scheme 1.

In conclusion, the bromide/bromate couple in aqueous acidic medium serves as an efficient and green reagent for the synthesis of the α-bromoketone by direct oxybromination of olefins avoiding



Scheme 1. Proposal of the mechanism for the synthesis of α-bromoketones from olefins.

hazardous molecular bromine. In addition, this procedure offers significant improvements with regard to reaction conditions (room temperature), good yields, and user-friendly operations compared to conventional methods. These results also highlight the significant scope for the synthesis of α-bromoketones from easily accessible olefins, which is inadequately reported in the literature.

Acknowledgment

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Supplementary data

Characterization data for products at entries 4, 10, 11 and 13–18 in Table 2. Copies of ^{1}H NMR and ^{13}C NMR of all products listed in Table 2. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.047.

References and notes

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9. (***Caution***: All the compounds are lachrymators and proper care should be taken while handling.) *General procedure for the synthesis of α-bromoketone from olefins. Representative procedure for 2-bromo-1-phenyl-ethanone* (Table 1, *entry* 1): To a solution of styrene (1.0 g, 9.6 mmol) in 1,4-dioxane (5.0 mL) was added an aqueous solution (20 ml) containing a 2:1 mole ratio of NaBr (1.38 g, 13.4 mmol)—$NaBrO_3$ (1.01 g, 6.7 mmol) (2.1 equiv) reagent at room temperature. To the above mixture, 98% sulfuric acid (10.5 mmol) was added slowly under stirring at room temperature during 2.5 h. After complete addition of the acid, stirring was continued for further 4 h (TLC). The product was extracted with CH_2Cl_2 (3 × 25 ml). The combined organic layers were washed with aqueous $Na_2S_2O_3$ and dried over Na_2SO_4. Evaporation of solvent left the crude product which was purified by column chromatography over silica gel (ethyl acetate–hexane 5:95) to afford the pure white solid product (1.15 g, 5.76 mmol) 2-bromo-1-phenyl-ethanone **3** in 60% yield; melting point 48 °C, (Lit 48.8–49.3 °C).[10] The side products, styrene bromohydrin **4** (0.31 g, 12%) and styrene dibromide **5** (0.022 g, 1%) were also obtained. The spectroscopic data (IR, ^{1}H NMR and ^{13}C NMR) are in good agreement with the reported values.[10]
2-bromo-1-(4-*tert*-butylphenyl) ethanone (Table 2, entry 4): Yellow oil. IR: ν_{max} (Neat). 3042, 2965, 2870, 1680, 1605, 1566, 1465, 1428, 1407, 1365, 1284, 1194, 1104, 1008, 992, 847, 733, 665, 643, 578. ^{1}H NMR ($CDCl_3$-500 MHz)—(δ): 1.32 (s,9H), 4.43 (s, 2H), 7.47 (d, 2H, J = 8.5 Hz), 7.91 (d, 2H, J = 8.5 Hz) ppm. ^{13}C NMR ($CDCl_3$-125 MHz) (δ): 30.9, 31.2, 35.1, 125.7, 128.8, 131.2, 157.6, 190.7 ppm. HRMS Calcd for $C_{12}H_{15}BrO$ [M+1]$^+$: 255.0384; Found: 255.0385.
1-Bromo-hexan-2-one (Table 2, entry 10): Colorless liquid. IR: ν_{max} (Neat). 2956, 2931, 2859, 1718, 1462, 1403, 1377, 1255, 1124, 1057, 758, 631. ^{1}H NMR ($CDCl_3$-500 MHz)—(δ): 0.66 (s, 3H), 1.08 (d, 2H, J = 5.0 Hz), 1.34 (s, 2H), 2.40 (s, 2H), 3.65 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$-125 MHz) (δ): 13.7, 22.1, 25.8, 34.4, 39.5, 202.1 ppm. HRMS Calcd for $C_6H_{11}BrO$ [M+1]$^+$: 179.0071; Found: 179.0072.
1-Bromo-octan-2-one (Table 2, entry 11): yellow oil. IR: ν_{max} (Neat). 2930, 2858, 1716, 1464, 1213, 1055, 878, 671, 487. ^{1}H NMR ($CDCl_3$-500 MHz)—(δ) = 0.89 (s, 3H), 1.29 (s, 6H), 1.61 (s, 2H), 2.65 (s, 2H), 3.89 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$-125 MHz) (δ): 13.9, 22.4, 23.8, 28.6, 31.4, 34.3, 39.8, 202.2 ppm. LRMS Calcd for $C_8H_{15}BrO$ [M]$^+$: 207.0384; Found: 207.0385.
1-Bromo-decan-2-one (Table 2, entry 13): Pale yellow oil. IR: ν_{max} (Neat). 2928, 2857, 1719, 1462, 1401, 1065, 894, 634. ^{1}H NMR ($CDCl_3$-500 MHz)—(δ): 0.87 (s, 3H), 1.29 (d, 10H, J = 4 Hz), 1.61 (t, 2H, J = 7 Hz), 2.64 (t, 2H, J = 7 Hz), 3.89 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$-125 MHz) (δ): 14.0, 22.6, 23.8, 29.0, 29.2, 31.7, 34.3, 39.8, 202.1 ppm. HRMS Calcd for $C_{10}H_{19}BrO$ [M]$^+$: 235.0697; Found: 235.0698.
1-Bromo-undecan-2-one (Table 2, entry **14**): White crystalline solid melting point observed 40-41 °C. IR: ν_{max} (Neat). 2925, 2854, 1719,1468, 1406, 1243, 1128, 1086, 1038, 719, 693, 638, 469. ^{1}H NMR ($CDCl_3$-500 MHz)—(δ): 0.87 (t, 3H, J = 7 Hz), 1.28 (t, 12H, J = 6 Hz), 1.62 (t, 2H, J = 3.5 Hz), 2.64 (t, 2H, J = 7 Hz), 3.88 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$-125 MHz) (δ): 14.1, 22.6, 23.8, 29.0,29.2, 29.3, 29.4, 31.8, 34.3, 39.8, 202.3 ppm. Elemental Anal. Calcd for $C_{11}H_{21}BrO$ is C, 53.02; H, 8.49. Found: C, 53.26; H, 9.21. LRMS Calcd for $C_{11}H_{21}BrO$ [M]$^+$: 249.19; Found: 248.67.
1-Bromo-dodecan-2-one (Table 2, entry **15**): White crystalline solid melting point observed 41–42 °C. IR: ν_{max} (Neat). 2925, 2855, 1720, 1468, 1408, 1238, 1128, 1090, 1049, 719, 693, 639. ^{1}H NMR ($CDCl_3$-500 MHz)—(δ): 0.88 (t, 3H, J = 6 Hz), 1.27 (s, 14H), 1.61 (t, 2H, J = 7 Hz), 2.64 (t, 2H, J = 7 Hz), 3.89 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$-125 MHz) (δ): 14.1, 22.7, 23.8, 29.0, 29.3, 29.4, 29.6, 31.9, 34.3, 39.8, 202.2 ppm. Elemental Anal. Calcd for $C_{12}H_{23}BrO$ is C, 54.76; H, 8.81. Found: C, 55.03; H, 9.09. LRMS Calcd for $C_{12}H_{23}BrO$ [M]$^+$: 263.21; Found: 262.68.
1-Bromo-tetradecan-2-one (Table 2, entry 16): White solid melting point observed 54–55 °C. IR: ν_{max} (Neat). 2925, 2853, 1720, 1469, 1410, 1249, 1129, 1097, 1061, 719, 640. ^{1}H NMR ($CDCl_3$-500 MHz)—(δ): 0.88 (t, 3H, J = 5 Hz), 1.25 (s, 18H), 1.61 (t, 2H, J = 7.5 Hz), 2.64 (t, 2H, J = 7 Hz), 3.89 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$-125 MHz) (δ): 14.1, 22.7, 23.8, 29.0, 29.36, 29.38, 29.4, 29.62, 29.66, 29.67, 31.9, 34.3, 39.8, 202.2 ppm. Elemental Anal. Calcd for $C_{14}H_{27}BrO$ is C, 57.73; H, 9.34. Found: C, 57.98; H, 7.91. LRMS Calcd for $C_{14}H_{27}BrO$ [M]$^+$: 291.27; Found: 290.74.
1-Bromo-hexadecan-2-one (Table 2, entry 17): White solid melting point observed 58–59 °C. IR: ν_{max} (Neat). 2923, 2822, 1720, 1469, 1409, 1254, 1129, 1090, 1034, 718, 640. ^{1}H NMR ($CDCl_3$-500 MHz)—(δ): 0.88 (t, 3H, J = 6 Hz), 1.25 (s, 22H), 1.61 (d, 2H, J = 6 Hz), 2.64 (t, 2H, J = 7 Hz), 3.88 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$): (δ): 14.1, 22.7, 23.8, 29.0, 29.3, 29.4, 29.6, 31.9, 34.3, 39.8, 202.2 ppm. Elemental Anal. Calcd for $C_{16}H_{31}BrO$ is C, 60.18; H, 9.79. Found: C, 60.23; H, 10.72. LRMS Calcd for $C_{16}H_{31}BrO$ [M+ Na]$^+$: 342.31; Found: 341.46.
1-Bromo-octadecan-2-one (Table 2, entry **18**): White solid melting point observed 62-63 °C. IR: ν_{max} (Neat). 2922, 2852, 1725, 1465, 1389, 1249, 1081, 724, 638. ^{1}H NMR ($CDCl_3$-500 MHz)—(δ): 0.88 (t, 3H, J = 6 Hz), 1.25 (s, 26H), 1.60 (d, 2H, J = 6.5 Hz), 2.64 (t, 2H, J = 7.5 Hz), 3.88 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$): (δ): 14.1, 22.7, 23.8, 29.0, 29.35, 29.39, 29.4, 29.61, 29.67, 29.69, 29.7, 31.9, 34.3, 39.8, 202.2 ppm. Elemental Anal. Calcd for $C_{18}H_{35}BrO$ is C, 62.24; H, 10.16. Found: C, 62.50; H, 9.93. LRMS Calcd for $C_{18}H_{35}BrO$ [M+Na]$^+$: 370.36; Found: 369.47.
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