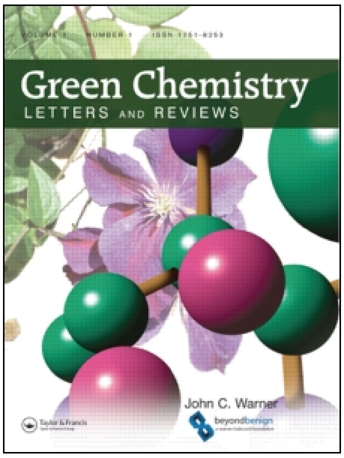

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An eco-friendly oxidative bromination of alkanones by an aqueous grinding technique

K. Jakhar[a]; J. K. Makrandi[a]
[a] Department of Chemistry, M. D. University, Rohtak, India

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ORIGINAL ARTICLE

An eco-friendly oxidative bromination of alkanones by an aqueous grinding technique

K. Jakhar and J.K. Makrandi*

Department of Chemistry, M. D. University, Rohtak, India

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α-Bromoalkanones have been synthesized by reacting alkanones with ammonium bromide and ammonium persulfate in high yields using an aqueous grinding technique.

Keywords: grinding technique; ammonium bromide; ammonium persulfate; α-bromoalkanone

Introduction

Bromination is usually used as an important reaction to form the intermediates which are further used to achieve desired complex functionalities and structures. α-Bromoalkanones are the important synthons used for the synthesis of various biologically active heterocyclic compounds which include benzofurans (*1*), aurones (*2*), 3-bromoflavones (*3*), thiazoles (*4*), thiadiazines (*5*), thiadiazoles (*6*).

α-Bromoalkanones are generally obtained by the reaction of alkanones with various reagents such as bromine (*7*), copper (II) bromide (*8*), dioxane dibromide (*9*), tetrabutylammonium tribromide (*10*), polymer-supported pyridinium bromide perbromide (*11*) and N-bromosuccinimide (*12*). For the bromination of organic compounds, oxidative bromination has also been adopted where a halogen acid or salt of acid is used in combination with an oxidant such as KBr-oxone (*13*), NH_4Br-hydrogen peroxide (*14*) and LiBr-peroxydisulphate (*15*) which generates a bromonium ion *in situ*. Several reports have also appeared on oxidative halogenations using catalysts such as V_2O_5 (*16*), NH_4VO_3, Na_2MO_4 (*17*), alkali bromates (*18*), sodium chlorite (*19*), and dil. HNO_3 (*20*). Oxidative bromination has also been studied using phase transfer catalysis (*3*) and microwave irradiations (*21*) and the reactions were found to be much more efficient.

The use of molecular bromine causes a serious threat to the environment and human health due to its toxicity and corroding nature. In addition, only one bromine atom is used up in the reaction while the other escapes as HBr (*22*). Use of other reagents requires organic solvents as medium of the reaction which is considered to be hazardous to human health and environment due to their volatile nature (*23*).

Today, much effort is being made to develop the procedures that avoid the use of hazardous chemicals and organic solvents to protect our environment. The synthesis of organic compounds using grinding technique under solvent-free conditions has received much attention (*24*) as it provides manipulative simplicity, greater selectivity, lesser reaction periods and higher yields.

Results and discussion

Keeping in mind the importance of alpha-bromoalkanones in the synthesis of organic compounds, we wish to report a method for α-bromination of alkanones which involves the grinding of alkanones with ammonium bromide and ammonium persulfate under slightly moist conditions in a mortar by a pestle (Scheme 1). The solid bromo compound separates out on dilution with water, and therefore avoids the use of organic solvents for extraction. To fine-tune the amount of ammonium bromide and ammonium persulfate required for the reaction to occur, the concentration of the reagents were varied. It was found that the best results could be obtained when 2 molar equivalent of ammonium bromide and 2.5 molar equivalent of ammonium persulfate were used.

The validity of the reaction was established by converting differently substituted acetophenones into their α-bromo derivatives (Table 1). The present method was also successfully used for the preparation of 3-bromoacetyl coumarin, 2-bromoacetyl benzofuran and 3-bromoacetyl cinnoline; the required intermediates for the synthesis of various bridgehead nitrogen containing fused heterocyclic systems (*25*–

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*Corresponding author. Email: jagdish_chem2000@rediffmail.com

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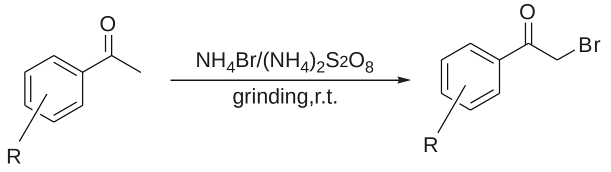
27). The identity of compounds was confirmed from their IR and ^{1}H NMR spectra and melting point comparison with literature values.

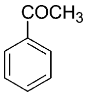
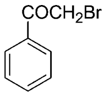
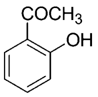
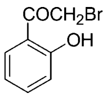
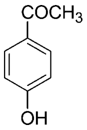
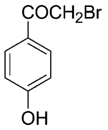
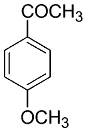
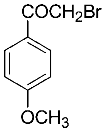
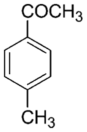
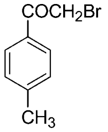
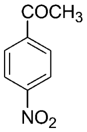
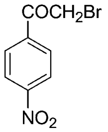
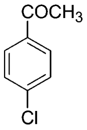
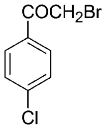
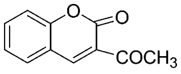
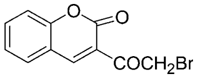
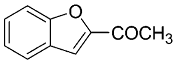
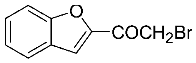
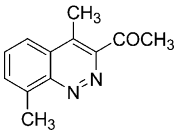
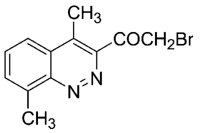


Scheme 1. General procedure for bromination of alkanones.

Experimental section

Melting points were determined in open capillary tubes and are uncorrected. IR spectra (KBr) were recorded in a Perkin-Elmer spectrum BX series FT-

Table 1. Bromination of organic compounds using NH_4Br and $(NH_4)_2S_2O_8$.

Entry	Substrate	Product	Time (min)$^{a+b}$	Yield (%)	M.P. (°C)	Lit. M.P. (°C)
1			15+20	84	47–49	48–51(*28*)
2			15+25	90	38–39	39–41(*28*)
3			15+20	83	126–128	128–129(*28*)
4			15+20	87	68–70	69–71(*28*)
5			15+25	86	44–47	45–48(*28*)
6			15+25	88	99–100	100(*28*)
7			15+20	91	95–97	96–97(*28*)
8			15+15	90	163–165	164–168(*25*)
9			15+15	88	88–90	90–91(*26*)
10			15+10	92	119–120	120–122(*27*)

[a] Grinding time.

[b] Time for which reaction mixture was kept at room temperature.

IR spectrophotometer and ^{1}H NMR on Bruker Avance II 400 MHz spectrometer using tetramethylsilane as an internal standard.

General procedure

A mixture of alkanone (1 mmol), ammonium bromide (2 mmol) and ammonium persulfate (2.5 mmol) moist with 6–10 drops of water was ground in a mortar by a pestle at room temperature for 15 minutes. The reaction mixture was kept at room temperature for 10–25 minutes until the completion of reaction which was checked by thin layer chromatography. The reaction mixture was diluted with ice cold water. A solid precipitated upon dilution. The solid was collected by vacuum filtration and recrystallized from ethanol.

3-(2-bromoacetyl) coumarin (Table 1, Entry 8)

IR (KBr) 1686 and 1729 (C = O); ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 4.75$ (s, 2H, CH_2); 7.37–7.42 (m, 2H, ArH); 7.69–7.73 (m, 2H, ArH); 8.64 (s, 1H, ArH).

2-(2-bromoacetyl) benzofuran (Table 1, Entry 9)

IR (KBr) 1688 (C = O); ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 4.44$ (s, 2H, CH_2); 7.32–7.36 and 7.49–7.54 (m. 2H, ArH); 7.58–7.60 (d, 1H, ArH, J = 8.4); 7.66 (s, 1H, ArH); 7.72–7.74 (d, 1H, ArH, J = 8.4).

3-(2-bromoacetyl)-4, 8-dimethyl cinnoline (Table 1, Entry 10)

IR (KBr) 1701 (C = O); ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 2.79$ (s, 3H, CH_3); 3.03 (s, 3H, CH_3); 5.44 (s, 2H, CH_2); 6.2 (d, 1H, ArH, J = 8.3); 6.4 (s, 1H, ArH); 9.4 (d, 1H, ArH, J = 8.4).

Conclusion

In conclusion, we have described a simple, highly efficient and economical protocol for the bromination of alkanones under slightly aqueous conditions by grinding technique.

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