Balaji B. Totawar, Pramod S. Kulkarni and Zubaidha K. Pudukulathan*

An improved and sustainable approach for the synthesis of α,β-dibromo ketones using ceric ammonium nitrate and ammonium bromide

DOI 10.1515/gps-2015-0097
Received October 3, 2015; accepted November 24, 2015; previously published online January 23, 2016

Abstract: A simple and environmentally benign procedure for the bromination of substituted α,β-unsaturated ketones in good yield has been described using ammonium bromide as a brominating agent and ceric ammonium nitrate (CAN) as a single-electron oxidant to afford α,β-dibromoketones. The reaction involves C-Br bond formation by radical method generated by CAN. The reaction can be carried out by either at room temperature, stirring in solvent CH_3CN or under aqueous moist condition with few drops of water by manual grinding in a mortar and pestle.

Keywords: α,β-unsaturated ketone; ammonium bromide; bromination; CAN; dibromo ketone; grinding; sustainable approach.

1 Introduction

The central theme of organic synthesis is carbon-carbon and carbon-heteroatom bond-forming reactions which comprise a major progress in modern synthesis, and this progress in turn results in development of novel methodologies. The application of carbon-centered radicals resulting from redox processes mediated by high-valent metal salts such as Mn (III), Co (III), V (V) and Ce (IV) has emerged as a powerful tool for carbon-carbon bond formation in recent years [1, 2]. The use of Ce (IV) reagents as convenient oxidants for a variety of substrates is well established [3–5]. Recently, C-C [6–9] and C-heteroatom [10–13] bond-forming reactions mediated by ceric ammonium nitrate (CAN) have been the subject of considerable interest [8–13]. One-electron oxidant CAN is one of the most important reagents, which appeals more and more with explored findings, as well as due to its use as Lewis acid catalyst from the group of lanthanide (IV) complexes in organic synthesis [8]. For the generation of radicals, CAN has been found to have the chemically upper hand in many respects to widely employed manganese triacetate [14]. CAN has some auxiliary advantages in terms of low toxicity, cost, solubility in many organic solvents and stability in air.

Organic bromine compounds have traditionally played an important role as intermediates in the production of agrochemicals, pharmaceuticals and dyes and others [15, 16]; some bromine compounds have been used as flame retardant and disinfectant. Bromination [17, 18] is termed as an important organic transformation, and bromination-debromination strategy for the protection-deprotection of double bonds has a substantial role in organic synthesis. Also, dibromoalkanes are important compounds widely used as versatile synthetic intermediates in a considerable number of useful transformations and for the protection-deprotection of unsaturated hydrocarbons [19–23]. The conventional method for bromination involves the use of bromine in chlorinated solvents [24], and unfortunately, a vast number of reported procedures employ highly polluting reaction conditions. In this context, several alternate green brominating agents have been reported to avoid the use of hazardous molecular bromine. Some of the methods worth mentioning are I_2O_5-KBr [25], potassium and ammonium halides [26] as the bromine source, oxybromination of activated aromatic compounds catalyzed by ammonium molybdate [27], environmentally benign electrophilic and radical bromination "in water": H_2O_2-HBr system [28], NH_4Br-oxone [29, 30], solvent-free bromination reactions with sodium bromide and oxone [31], bromination of chalcones using grinding technique [32], action of tetrabutylammonium tribromide on para-substituted chalcones in protic and aprotic media [33], in situ generated bromine under oxidative conditions [34], pyridiniumbromide-perbromide, quaternary ammonium tribromide or tribromide perbromide [35]. Though

---

***Corresponding author: Zubaidha K. Pudukulathan,** School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, Maharashtra 431606, India, e-mail: pzubaidha20001@yahoo.co.in
Balaji B. Totawar: School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, Maharashtra 431606, India
Pramod S. Kulkarni: Department of Chemistry, Hutatma Rajguru Mahavidyalaya Rajgurunagar, Pune, Maharashtra 410505, India

the search for sustainable protocol has led to tremendous progress in this area, most of the methods suffer from use of acid or organic solvents and are time consuming. Herein we present two approaches for bromination of enones under mild conditions and hence a step forward towards sustainable method development in tune with the current research scenario.

2 Materials and methods

Melting points were recorded by open capillary method on an electrothermal melting point apparatus and are uncorrected. The NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as an internal standard on Agilent VnmrJ 3.2 Spectroscopy 400/54 ASP, USA; IR spectra were recorded on a FT-IR 3.1 Win-BOMEM, Italy, apparatus. Flash chromatography was performed on thin layer chromatography (TLC) grade silica gel, and analytical TLC was performed on Merck silica gel 60 F254 pre-coated plates. The spots were visualized under UV light or by iodine vapors. Solvents were distilled before use. Ammonium bromide and ceric ammonium nitrate were procured from SD Fine chemicals, Mumbai, India, and in the preparation of chalcones we used benzaldehyde produced by Rankem, New Delhi, acetophenone from Hi-media, Mumbai, and NaOH from SD Fine Chemicals. All other commercial substrates were purchased from standard sources, and most of them were from SD Fine chemicals and were used as such.

2.1 Experimental procedure

2.1.1 Method A: To a mixture of α,β-unsaturated carbonyl compound (1 mmol) and NH_4Br (2 mmol) in acetonitrle (3–5 ml), CAN (2 mmol) was added at room temperature with stirring. After completion of the reaction (monitored by TLC, in 30–35 min), red orange color of reaction mixture decolorizes with formation of white solid of ceric (III) ammonium nitrate. The solid was filtered off and washed with chloroform. The combined organic layer was rotaevaporated under reduced pressure, and the residue was crystallized from ethanol.

2.1.2 Method B: A mixture of NH_4Br (2 mmol) and α,β-unsaturated carbonyl compound (1 mmol) was powdered in a mortar with pestle, and CAN (2 mmol) was added with grinding. The resulting mixture was ground for 5 min till it became sticky. Then the sticky mass was transformed to gel by addition of a few drops of water and left for 5 min. With one final grinding, the mixture was extracted with chloroform, and the combined organic layer was dried over sodium sulfate and concentrated under a vacuum. The residue obtained was crystallized from ethanol, and the product thus obtained was reasonably pure for all practical purposes.

2.2 Spectral analysis of synthesized compounds

2,3-Dichloro-1,3-diphenylpropan-1-one (**1a**): Yield: By method A: 52% and method B: 00%; IR: 1690, 796, 780; ^1H NMR ($CDCl_3$): δ 5.78 (d, *J*=12.4 Hz, 1Hβ), 5.84 (d, *J*=12.4 Hz, 1Hα), 7.41–7.53(m, 8H), 8.01 (d, *J*=8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 52.8 (Cβ), 72.1 (Cα), 128.2, 128.9, 129.3, 129.5, 134.0, 135.0, 138.3, 191.9 (C=O).

3,4-Dibromobutan-2-one (**2a**): Yield: By method A: 67% and method B: 65%; IR: 1678, 710, 675, cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.36 (s, 3H, 1H), 3.64 (dd, *J*=8, 12 Hz, 1H), 3.90 (dd, *J*=8, 12 Hz, 1H), 4.51 (dd, *J*=8, 12 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 25.8, 28.1, 61.9, 198.2 (C=O).

3,4-Dibromo-4-phenylbutan-2-one (**2b**): Yield: By method A: 93% and method B: 91%; IR: 1662, 720, 712; ^1H NMR ($CDCl_3$): δ 2.47 (s, 3H), 4.93 (d, *J*=12 Hz, 1Hβ), 5.31 (d, *J*=12 Hz, 1Hα), 7.41 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 27.1, 49.5 (Cβ), 52.7 (Cα), 128.9, 129.3, 137.7, 191.4 (C=O).

2,3-Dibromo-1,3-diphenylpropan-1-one (**2c**): Yield: By method A: 91% and method B: 90%; IR: 1646, 725, 715; ^1H NMR ($CDCl_3$): δ 5.85 (d, *J*=12 Hz, 1Hβ), 5.66 (d, *J*=12 Hz, 1Hα), 7.26–7.67 (m, 8H), 8.09 (d, *J*=8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 46.8 (Cβ), 49.7 (Cα), 128.3, 128.9, 129.0, 129.3, 134.2, 191.2 (C=O).

2,3-Dibromo-3-phenyl-1-p-tolylpropan-1-one (**2d**): Yield: By method A: 94% and method B: 90%; IR: 1638, 727, 715; ^1H NMR ($CDCl_3$): δ 2.41 (s, 3H), 5.49 (d, *J*=12 Hz, 1Hβ), 5.62 (d, *J*=12 Hz, 1Hα), 7.46 (m, 5H), 7.10 (d, *J*=8 Hz, 2H), 7.91 (d, *J*=8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 21.32, 44.7 (Cβ), 54.1 (Cα), 127.1, 128.0, 128.3, 128.8, 129.2, 135.0, 135.6, 139.9 ($C\text{-}CH_3$), 189.1 (C=O).

2,3-Dibromo-1-(4-methoxyphenyl)-3-phenylpropan-1-one (**2e**): Yield: By method A: 20% and method B: 75%; IR: 1635, 1112, 727, 718; ^1H NMR ($CDCl_3$): δ 3.89 (s, 3H), 5.64 (d, *J*=12 Hz, 1Hβ), 5.80 (d, *J*=12 Hz, 1Hα), 7.01 (dd, *J*=8, 8 Hz, 2H), 7.39–7.43 (m, 3H), 7.52 (d, *J*=8 Hz, 2H), 8.09 (dd, *J*=8, 8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 46.7 (Cβ), 50.0 (Cα), 55.6 ($O\text{-}CH_3$), 114.2, 127.1, 128.3, 128.8, 129.2, 131.3, 138.4, 164.4 (C4′), 189.1 (C=O).

2,3-Dibromo-1-(4-nitrophenyl)-3-phenylpropan-1-one (**2f**): Yield: By method A: 83% and method B: 79%; IR: 1640, 1180, 722, 716; ^1H NMR ($CDCl_3$): δ 5.59 (d, *J*=11.6 Hz, 1Hβ), 5.71 (d, *J*=11.6 Hz, 1Hα), 7.34–7.44 (m, 5H), 7.69 (d, *J*=8 Hz, 2H), 8.01 (d, *J*=8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 46.0 (Cβ), 52.9 (Cα), 126.8, 128.4, 128.9, 129.2, 135.2, 136.9, 139.9, 153.2 (C4′), 191.1 (C=O).

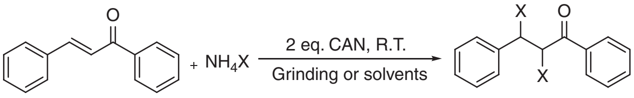
2,3-Dibromo-1-(4-fluorophenyl)-3-phenylpropan-1-one (**2g**): Yield: By method A: 87% and method B: 82%; IR: 1632, 1235, 722, 717; ^1H NMR ($CDCl_3$): δ 5.66 (d, *J*=11.2 Hz, 1Hβ), 5.73 (d, *J*=11.2 Hz, 1Hα), 7.30 (m, 3H), 7.36 (d, *J*=8.4 Hz, 2H), 7.53 (m, 2H), 8.15 (d, *J*=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 46.1 (Cβ), 51.2 (Cα), 117.1, 128.7, 129.7, 129.9, 130.8, 134.8, 136.8, 165.7 (C4′), 189.7 (C=O).

2,3-Dibromo-1-(4-chlorophenyl)-3-phenylpropan-1-one (**2h**): Yield: By method A: 93% and method B: 90%; IR: 1634, 780, 725, 720; ^1H NMR ($CDCl_3$): δ 5.66 (d, *J*=12.4 Hz, 1Hβ), 5.78 (d, *J*=12.4 Hz, 1Hα), 7.34 (m, 5H), 7.59 (d, *J*=8 Hz, 2H), 7.87 (d, *J*=8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 46.1 (Cβ), 59.2 (Cα), 128.1, 128.7, 129.2, 129.4, 131.7, 135.2, 137.9, 140.7 (C4′), 189.0 (C=O).

2,3-Dibromo-1-(4-bromophenyl)-3-phenylpropan-1-one (**2i**): Yield: By method A: 91% and method B: 89%; IR: 1633, 726, 720, 630; ^1H NMR ($CDCl_3$): δ 5.63 (d, *J*=12 Hz, 1Hβ), 5.77 (d, *J*=12 Hz, 1Hα), 7.52 (m, 5H), 7.70 (d, *J*=8 Hz, 2H), 7.97 (d, *J*=8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 46.5 (Cβ), 49.6 (Cα), 128.3, 128.8, 129.3, 129.5, 130.3, 132.3, 132.9, 137.9 (C4′), 190.2 (C=O).

2,3-Dibromo-1-(3-chlorophenyl)-3-phenylpropan-1-one (**2j**): Yield: By method A: 87% and method B: 82%; IR: 1630, 770, 726, 720; ^1H NMR ($CDCl_3$): δ 5.62 (d, *J*=12 Hz, 1Hβ), 5.76 (d, *J*=12 Hz, 1Hα), 7.52 (m, 6H), 8.03 (d, *J*=8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 46.7 (Cβ), 49.6 (Cα), 128.3, 128.9, 129.0, 129.1, 129.9, 130.2, 132.9, 138.0 (C4′), 191.1 (C=O).

2,3-Dibromo-1,3-bis(4-fluorophenyl)propan-1-one (**2k**): Yield: By method A: 92% and method B: 90%; IR: 1631, 1290, 729, 722; ^1H NMR ($CDCl_3$): δ 5.65 (d, *J*=12 Hz, 1Hβ), 5.72 (d, *J*=12 Hz, 1Hα), 7.31 (m, 4H), 7.40 (d, *J*=8.4 Hz, 2H), 7.89 (d, *J*=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 45.7 (Cβ), 50.6 (Cα), 116.9, 117.7, 130.1, 130.8, 131.2, 134.2, 164.1, 165.9, 190.1 (C=O).

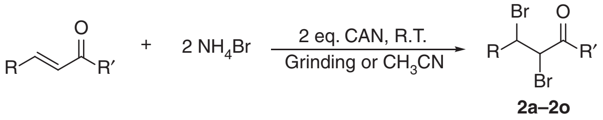


Scheme 1: Reaction of chalcone with different ammonium halides.

Table 1: Effect of solvent on time and yield in the bromination of chalcone with NH_4Br and CAN.[a]

Sr. No.	Solvent	Time	Temperature	% Yield
1	CH_2Cl_2	5–6 h	RT (25–27°C)	45
2	$CHCl_3$	5–6 h	RT (25–27°C)	52
3	Ethyl acetate	12 h	RT (25–27°C)	68
4	Methanol	2.5 h	RT (25–27°C)	72
5	Ethanol	2 h	RT (25–27°C)	76
6	CH_3CN	35–40 min	RT (25–27°C)	91
7	DMF	50–55 min	RT (25–27°C)	84
8	DMSO	50–55 min	RT (25–27°C)	86
9	Water	12 h	Reflux	55
10	Grinding	20–25 min	RT (25–27°C)	90

[a] Study of reaction between chalcone and ammonium bromide was carried out with almost all solvents reported in literature.



Scheme 2: Synthesis of dibromo chalcone using ammonium bromide and CAN.

2,3-Dibromo-3-(2-fluorophenyl)-1-(4-fluorophenyl)propan-1-one (**2l**): Yield: By method A: 87% and method B: 80%; IR: 1631, 1280, 720, 724; ^{1}H NMR ($CDCl_3$): δ 5.66 (d, *J*=12 Hz, 1Hβ), 5.77 (d, *J*=12 Hz, 1Hα), 7.31 (m, 6H), 7.89 (d, *J*=8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 46.2 (Cβ), 52.1 (Cα), 116.2, 117.2, 126.4, 129.6, 129.9, 130.7, 133.3, 161.2, 165.2, 189.7 (C=O).

2,3-Dibromo-1-phenyl-3-p-tolylpropan-1-one (**2m**): Yield: By method A: 91% and method B: 88%; IR: 1629, 724, 718; ^{1}H NMR ($CDCl_3$): δ 5.66 (d, *J*=12 Hz, 1Hβ), 5.77 (d, *J*=12 Hz, 1Hα), 7.31 (m, 6H), 7.89 (d, *J*=8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 21.5, 46.2 (Cβ), 49.6 (Cα), 127.9, 128.4, 128.9, 129.1, 129.9, 135.2, 136.8, 140.1, 190.8 (C=O).

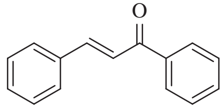
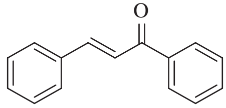
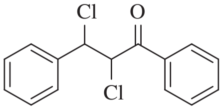
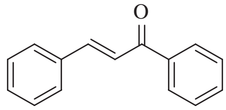
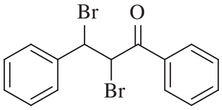
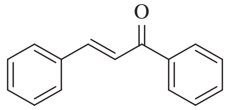
2,3-Dibromo-3-(4-methoxyphenyl)-1-phenylpropan-1-one (**2n**): Yield: By method A: 20% and method B: 75%; IR: 1632, 1105, 728, 718; ^{1}H NMR ($CDCl_3$): δ 3.81 (s, 3H), 5.61 (d, *J*=12 Hz, 1Hβ), 5.73 (d, *J*=12 Hz, 1Hα), 6.95 (dd, *J*=8.8 Hz, 2H), 7.26 (dd, *J*=8,8 Hz, 2H), 7.63–7.51 (m, 3H), 7.87 (d, *J*=8 Hz, 2H) ^{13}C NMR ($CDCl_3$): δ 43.9 (Cβ), 49.2 (Cα), 55.1, 114.9, 128.2, 128.7, 131.0, 132.2, 134.1, 137.0, 160.1 (C4), 190.8 (C=O).

2,3-Dibromo-3-(4-nitrophenyl)-1-phenylpropan-1-one (**2o**): Yield: By method A: 83% and method B: 80%; IR: 1638, 1370, 722, 716; ^{1}H NMR ($CDCl_3$): δ 5.71 (d, *J*=12 Hz, 1Hβ), 5.63 (d, *J*=12 Hz, 1Hα), 7.71–7.31 (m, 5H), 7.24 (d, *J*=8.4 Hz, 2H), 8.10 (d, *J*=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 44.9 (Cβ), 50.9 (Cα), 124.7, 128.2, 128.6, 129.0, 129.5, 134.7, 136.3, 149.3 (C4), 190.8 (C=O).

3 Results and discussion

CAN in the presence of NH_4Br brings about bromination of enones and chalcones to afford the corresponding dibromide in good to excellent yields (Scheme 1).

Table 2: Halogenations of chalcones with CAN using different ammonium halides.[a]

Sr. No.	Substrate	Ammonium halide	Product	% Yield	
				Stirring with solvent A	Grinding with few drops of water B
1.		NH_4F	No reaction	No reaction	No reaction
2.		NH_4Cl	 **1a**	52	No reaction
3		NH_4Br	 **3c**	91	90
4		NH_4I	No reaction	No reaction	No reaction

[a] Halogenations of chalcone in CH_3CN with different ammonium halides were carried out under all possible conditions like mild heating and reflux to get good yields in minimum time, and the optimized results are presented here.

Table 3: Bromination of different α,β unsaturated ketones with NH$_4$Br and CAN.[a]

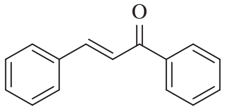
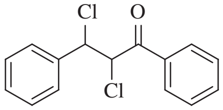
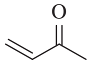
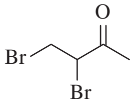
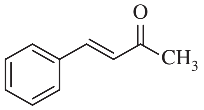
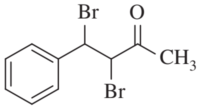
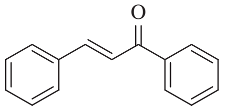
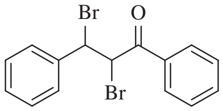
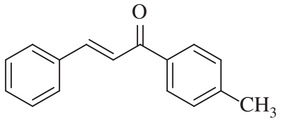
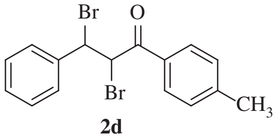
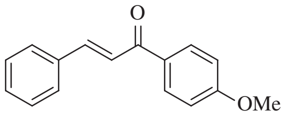
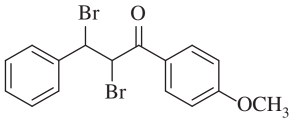
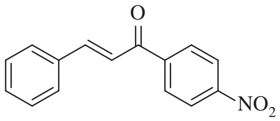
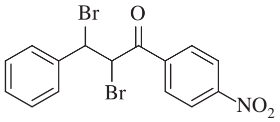
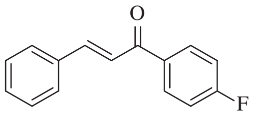
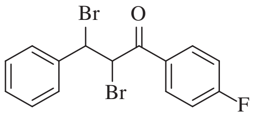
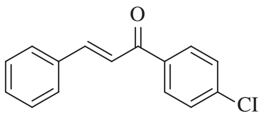
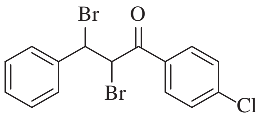
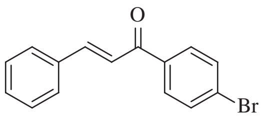
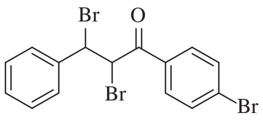
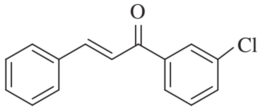
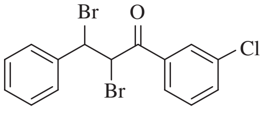
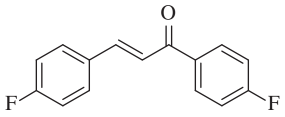
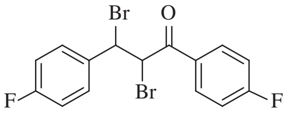
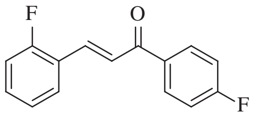
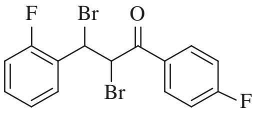
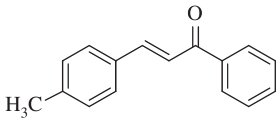
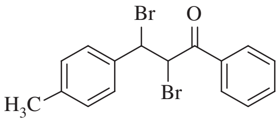
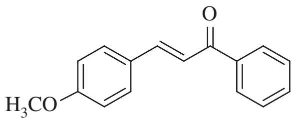
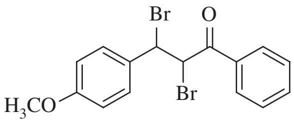
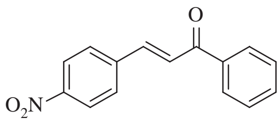
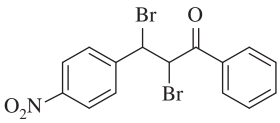
Sr. No.	Substrate	Product	% Yield[b]		Time		M. P. in °C
			Stirred in solvent	Grinding in mortar and pestle	Stirred in solvent	Grinding in mortar and pestle	
1		 **1a**	52	–	1 h	–	–
2		 **2a**	67	65	10 min	15–20 min	-
3		 **2b**	93	91	25–30 min	15–20 min	123–125
4		 **2c**	91	90	35–40 min	15–20 min	156–158
5		 **2d**	94	90	35–40 min	15–20 min	147–149
6		 **2e**	20	75	4 h	15–20 min	146–148
7		 **2f**	83	79	35–40 min	15–20 min	188–190
8		 **2g**	87	82	35–40 min	15–20 min	156–158
9		 **2h**	93	90	35–40 min	15–20 min	171–173
10		 **2i**	91	89	35–40 min	15–20 min	185–186

Table 3 (continued)

Sr. No.	Substrate	Product	% Yield[b]		Time		M. P. in °C
			Stirred in solvent	Grinding in mortar and pestle	Stirred in solvent	Grinding in mortar and pestle	
11		 **2j**	87	82	35–40 min	15–20 min	175–177
12		 **2k**	92	90	35–40 min	15–20 min	155–157
13		 **2l**	87	80	35–40 min	15–20 min	142–144
14		 **2m**	91	88	35–40 min	15–20 min	148–150
15		 **2n**	20	75	4 h	15–20 min	90–92
16		 **2o**	83	80	35–40 min	15–20 min	130–132

[a]Method A: Reaction was performed at room temperature (28–30°C) with two equivalent of CAN in acetonitrile.

Method B: The reaction was carried out by grinding the reactants with mortar and pestle.

[b]Yields refer to pure isolated products fully characterized by spectral and analytical methods.

As the nature of the solvent is expected to play a crucial role in bromination, the reaction has been studied in different solvents commonly employed for the same. Table 1 displays the different solvents employed and their effect on yield and time. The reaction proceeded in most of the solvents screened, and acetonitrile was found to be the solvent of choice to afford the dibromo compound in 90% yield within 30–35 min at room temperature. Also, the reaction proceeded in appreciable way in DMF/DMSO in terms of conversion and time required for completion. The best results were obtained in grinding method under moist conditions to the tune of 90% yield within 20–25 min.

Further, the applicability of the present conditions with other ammonium halides have been explored, and the results are presented in Table 2. As is obvious from the table, the present reaction conditions did not work with ammonium iodide and fluoride for the respective halogen addition in both the methods studied, while chlorination with ammonium chloride proceeded in moderate yield in acetonitrile, and no reaction was observed in the grinding method.

Having optimized the reaction conditions for bromination in solvent acetonitrile and by grinding method (Scheme 2), different substituted enones/chalcones were subjected to the reaction conditions, and the results are

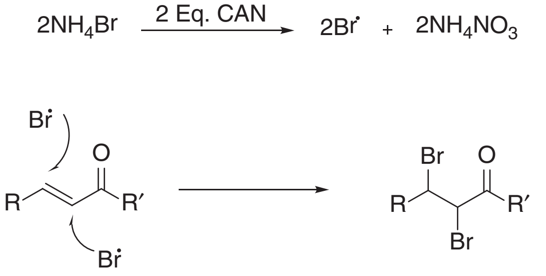


Figure 1: Mechanism for synthesis of dibromo chalcone using ammonium bromide and CAN.

presented in Table 3. Methyl vinyl ketone and benzylideneacetone (Table 3, entries 1 and 2) required less time for conversion compared to other substituted chalcones. As expected, the reaction proceeded better with chalcones bearing electron-donating substituents as compared to the ones bearing electron-withdrawing groups. Substituents on the aromatic ring exert effect on the conversion and time. It is remarkable that bromination of methoxy-substituted chalcones (Table 3, entries 5 and 14) proceeded well under grinding method, and the same in acetonitrile gave low yield of 20% after 11–12 h of stirring at room temperature .

Mechanistically, the bromination seems to proceed via addition of bromine radical formed by single-electron transfer to CAN (Figure 1).

4 Conclusion

As dibromoalkanes are important compounds widely used as versatile synthetic intermediates in a considerable number of useful transformations, their easy access by the present method would find widespread use in organic synthesis. The present work highlights the usefulness of CAN and NH_4Br as ecofriendly and mild reagent and salt, for economical, ecologically favorable bromination protocol with easy workup procedure coupled with short reaction times. The grinding method looks attractive in terms of conversion and reaction time, and the ease of handling cheaper ammonium bromide as a source of bromine makes the strategy an option of choice.

Acknowledgments: One of the authors, Balaji Totawar, would like to acknowledge UGC Scheme – Rajiv Gandhi National Fellowship support provided for SC/ST students.

Conflict of interest: The authors confirm that this article content has no conflicts of interest.

References

[1] De Klein WJ. In *Organic Synthesis by Oxidation with Metal Compounds*, Mijs, WJ, de Jonge, CRH, Eds., Plenum: New York, 1986, pp. 261–314.
[2] Iqbal J, Bhatia B, Nayyar N. *Chem. Rev.* 1994, 94, 519–564.
[3] Molander GA. *Chem. Rev.* 1992, 92, 29–68.
[4] Ho T. *Synthesis* 1973, 6, 347–354.
[5] Nair V, Panicker SB, Nair LG, George TG, Augustine A. *Synlett* 2003, 2, 156–165.
[6] Baciocchi E, Ruzziconi R. *J. Org. Chem.* 1991, 56, 4772–4778.
[7] Citterio A, Sebastiano R, Carvaya M. *J. Org.Chem.* 1991, 56, 5335–5341.
[8] Nair V, Mathew J, Prabhakaran J. *Chem. Soc.Rev.* 1997, 26, 127–132.
[9] Linker T, Hartmann K, Sommermann T, Scheutzov D, Ruckdeschel E. *Angew. Chem. Int. Ed. Engl.* 1996, 35, 1730–1732.
[10] Bosman C, Annibale AD, Resta S, Trogolo C. *Tetrahedron Lett.* 1994, 35, 6525–6528.
[11] Narasaka K, Mochizuk T, Hayakawa S. *Chem. Lett.* 1994, 23, 1705–1708.
[12] Nair V, George TG, Nair LG, Panicker S. *Tetrahedron Lett.* 1999, 40, 1195–1196.
[13] Trahanovsky WS, Robbins M. *J. Am. Chem. Soc.* 1971, 93, 5256–5258.
[14] Holzweber M, Schnürch M, Stanetty P. *Synlett* 2007, 19, 3016–3018.
[15] Gribble G. *Chem. Soc. Rev.* 1999, 28, 335–346.
[16] Ioffe D, Kampf A. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th ed., Kirk-Othmer, ed., John Wiley & Sons Inc: New York, 2004, Vol. 4, pp. 340.
[17] Kutsumura N, Niwa K, Saito T. *Org. Lett.* 2010, 12, 3316–3319.
[18] Kuang C, Yang Q, Senboku H, Tokuda M. *Tetrahedron* 2005, 61, 4043–4052.
[19] Maji T, Karmakar A, Reiser O. *J. Org. Chem.* 2011, 76, 736–739.
[20] Lee SH, Chang YM, Yoon C. *Bull. Korean Chem. Soc.* 2004, 25, 1723–1725.
[21] Totten LA, Jans U, Roberts A. *Environ. Sci. Technol.* 2001, 35, 2268–2274.
[22] Nair V, Panicker SB, Augusine A, George TG, Thomas S, Vairamani M. *Tetrahedron* 2001, 57, 7417–7422.
[23] Ranu BC, Guchhait SK, Sarkar A. *Chem. Commun.* 1998, 19, 2113–2114.
[24] Pavlinac J, Zupan M, Laali K, Stavber S. *Tetrahedron* 2009, 65, 5625–5665.
[25] Hou J, Li Z, Jia XD, Liu Z. *Synthetic Commun.* 2014, 44, 181–187.
[26] Kandepi VVKM, Narender N. *Synthesis* 2012, 44, 15–26.
[27] Choudary BM, Sudha Y, Reddy P. *Synlett* 1994, 6, 450.
[28] Podgoršek A, Stavber S, Zupan M, Iskra J. *Tetrahedron* 2009, 65, 4429.
[29] Kumar MA, Rohitha CN, Kulkarni SJ, Narender N. *Synthesis* 2010, 10, 1629.
[30] Naresh M, Kumar MA, Reddy MM, Swamy P, Nanubolu JB, Narender N. *Synthesis* 2013, 45, 1497.
[31] Wang GW, Gao J. *Green Chem.* 2012, 14, 1125.

[32] Jakhar K, Makrandi J. *Indian J. Chem.* 2013, 52B, 141–145.
[33] Berthelot J, Benamma Y, Desmazieres B. *Can. J. Chem.* 1995, 73, 1526–1530.
[34] Eissen M, Lenoir D. *Chem. Eur. J.* 2008, 14, 9830–9841.
[35] Subbarayappa A, Gadde R, Bedekar AV, Ghosh S, Ranu BC, Ghosh P. *Green Chem.* 2006, 8, 916–922.

Bionotes

Balaji B. Totawar

Balaji B. Totawar is a research scholar working for his doctoral degree at the School of Chemical Sciences, SRTM University, Nanded. He has been the recipient of a Rajiv Gandhi UGC fellowship, and his research interests include the development of CAN-mediated synthetic transformations.

Pramod S. Kulkarni

Pramod S. Kulkarni completed his PhD at Swami Ramanand Teerth Marathwada University, Nanded. He published five research papers in his PhD work. He is working as an Assistant Professor of Chemistry in Hutatma Rajguru Mahavidyalaya, Rajgurunagar Pune, India. He completed two minor research projects.

Zubaidha K. Pudukulathan

Zubaidha K. Pudukulathan is a Professor at the School of Chemical Sciences, SRTM University, Nanded. She has been working on the development of synthetic methodologies and design of enzyme inhibitors.