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An efficient bromination of alkenes using cerium(IV) ammonium nitrate (CAN) and potassium bromide

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Dedicated with best wishes to Professor James P. Kutney on the occasion of his 70th birthday.

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Abstract—Bromination of alkenes using a combination of potassium bromide and cerium(iv) ammonium nitrate (CAN) in a two phase system consisting of water and dichloromethane affords the corresponding dibromides in excellent yield. The reaction most likely involves the addition of the bromine radical generated from bromide ion by CAN and subsequent formation of the dibromide.

1. Introduction

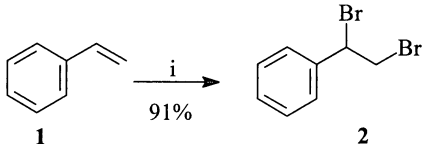
Recently, C–C bond forming reactions mediated by cerium(IV) ammonium nitrate (CAN) have been the subject of considerable interest.[1] Less attention however has been paid to the use of CAN in C-heteroatom bond formation despite the report of CAN mediated addition of azide to alkenes by Trahanovsky as early as 1971[2] and subsequent exploitation of the reaction in the synthesis of aminosugars by Lemieux et al.[3] Very recently we have observed the efficient thiocyanation of styrenes and indoles using NH_4SCN and CAN.[4–5] We have also reported the conversion of cinnamates to α-azidocinnamtes, cinnamic acids to β-azido styrenes[6] and styrenes to phenacyl azides and phenacyl thiocyanates.[7] It appeared that a similar strategy would be applicable for the bromination of alkenes without the direct use of bromine. The bromination of alkenes is an important organic transformation and it is worthy of note that protection and deprotection of double bonds via bromination–debromination strategy is finding increasing application in organic synthesis.[8] A number of protocols are available to achieve the bromination of alkenes.[9–13] Very recently, Fraser-Reid has reported the bromination of alkenyl glycosides using a combination of LiBr and $CuBr_2$.[14]

The bromination of alkenes using hydrobromic acid and *tert*-butyl hydroperoxide has also been reported.[15] In spite of the variety of reagents available for bromination, lack of selectivity and unwanted side reactions continue to be problems. In this context a search for mild, selective and easy-to-handle reagents assume importance.

2. Results and discussion

Against the background presented above, we have carried out a detailed investigation aimed at the bromination of various alkenes and our results are presented in this paper. Our studies were initiated by the treatment of styrene with potassium bromide and CAN in a two-phase system consisting of water and dichloromethane. A facile reaction occurred and the dibromide **2** was isolated in 91% yield (Scheme 1).

Mechanistically, by comparing the redox potentials of Br^-/Br and Ce (IV)/Ce (III)[16,17] it is reasonable to assume that bromide ion is undergoing oxidation to bromine radical by CAN and subsequent addition of the latter to the double bond producing a benzylic radical followed by trapping with another bromine radical (vide infra for a detailed discussion). A number of styrenes were subjected to similar reaction conditions and in all the cases, the dibromides were



1 **2**

Scheme 1. (i) CAN, KBr, H_2O, CH_2Cl_2, rt, 30 min.

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Table 1. Bromination of styrenes

Entry	Substrate	Reaction conditions	Product	Yield (%)
1	4-Methylstyrene (**3**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 35 min	1,2-Dibromo-(4-methyl)-phenyl ethane (**4**)	67
2	4-Chlorostyrene (**5**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 20 min	1,2-Dibromo-(4-chloro)-phenyl ethane (**6**)	85
3	β-Methylstyrene (**7**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 30 min	1,2-Dibromo-1-phenyl propane (**8**)	90
4	2-Vinylnaphthalene (**9**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 45 min	1,2-Dibromo-1-naphthyl ethane (**10**)	95

Table 2. Bromination of alkenes

Entry	Substrate	Reaction conditions	Product	Yield (%)
1	Cyclohexene (**11**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 20 min	1,2-Dibromocyclohexane (**12**)	65
2	Allylbenzene (**13**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 20 min	1,2-Dibromo-3-phenyl propane (**14**)	65
3	1-Octene (**15**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 35 min	1,2-Dibromooctane (**16**)	51
4	1-Hexene (**17**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 20 min	1,2-Dibromohexane (**18**)	82

Table 3. Bromination of α,β-unsaturated carbonyl compounds

Entry	Substrate	Reaction conditions	Product	Yield (%)
1	Methyl cinnamate (**19**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 50 min	2,3-Dibromo-3-phenyl methyl propanoate (**20**)	78
2	3,4-Dimethoxy ethylcinnamate (**21**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 20 min	2,3-Dibromo-3-(3′,4′-dimethoxy)-phenyl ethyl propanoate (**22**)	80
3	Benzylidene acetone (**23**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 20 min	3,4-Dibromo-4-phenyl butan-2-one (**24**)	81
4	Chalcone (**25**)	CAN, KBr, H_2O, CH_2Cl_2, rt, 20 min	2,3-Dibromo-1,3-diphenyl propan-1-one (**26**)	95

obtained in excellent yields. The results are summarized in Table 1.

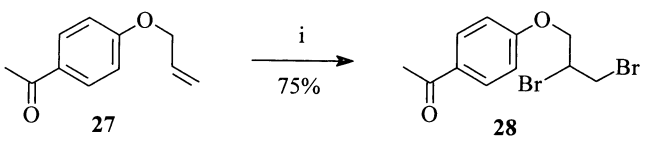
In order to assess the generality of the reaction, CAN mediated bromination was carried out with some representative alkenes and also with some α,β-unsaturated carbonyl compounds. In all the cases, the corresponding dibromides were obtained in high yields. Tables 2 and 3 summarize the results.

Since radical reactions are chemoselective in nature, it was of interest to probe the chemoselectivity of the CAN mediated bromination. When the allyl phenyl ether **27** was treated with KBr and CAN in a two-phase system consisting of water and dichloromethane under the reaction conditions described previously, the dibromide **28** was obtained in 75% yield (Scheme 2).

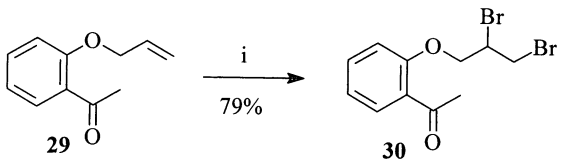
The isomeric compound **29** also on treatment with KBr and CAN underwent selective bromination yielding the dibromide **30** (Scheme 3).

In view of the facility and ease with which alkenes underwent CAN mediated bromination, it was of interest to explore the applicability of this reaction to acetylenes. With this objective, a number of acetylenes were treated under the reaction conditions used for the bromination of alkenes. The vicinal dibromoalkenes were obtained in excellent yields and the results are presented in Table 4. A mixture of isomers was obtained in one case and the ratio of the isomers was determined by GC–MS.

In order to gain an insight into the effect of solvent in these reactions, the reaction of styrene with potassium bromide and CAN in various solvents was studied. Interestingly, the product obtained was the nitrato bromide and phenacyl bromide (Scheme 4).

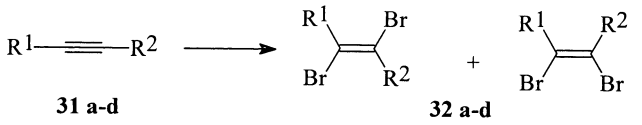


Scheme 2. (i) CAN, KBr, H_2O, CH_2Cl_2, rt, 30 min.



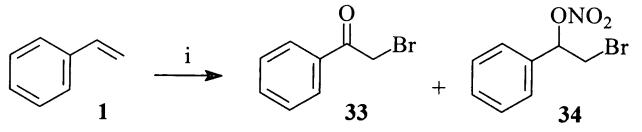
Scheme 3. (i) CAN, KBr, H_2O, CH_2Cl_2, rt, 30 min.

Table 4. Bromination of acetylenes (reaction conditions: KBr, CAN, H_2O, CH_2Cl_2, rt, 30 min)



31 a-d **32 a-d**

Entry	**31 a–d**	R^1	R^2	**32 a–d** (*E*/*Z*)	Yield (%)
1	**31a**	H	Ph	100/0	80
2	**31b**	Ph	Ph	80/20	94
3	**31c**	H	$(CH_2)_5CH_3$	100/0	79
4	**31d**	$(CH_2)_2CH_3$	$(CH_2)_2CH_3$	100/0	75

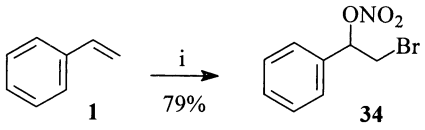


1 **33** **34**

Scheme 4. (i) CAN, KBr/LiBr, Solvent, rt.

Table 5. Effect of solvent in bromination reactions

Entry	Solvent	**33** (Yield, %)	**34** (Yield, %)	Reaction conditions
1	Aq. methanol	48	25	CAN, KBr, rt, 2 h
2	Aq. acetonitrile	35	35	CAN, KBr, rt, 1 h
3	Acetonitrile–acetic acid	12	68	CAN, LiBr, rt, 3 h
4	*tert*-Butanol	10	65	CAN, LiBr, rt, 6 h



1 **34**

Scheme 5. (i) CAN, LiBr, MeCN, Argon, rt, 2 h.

The results are presented in Table 5.

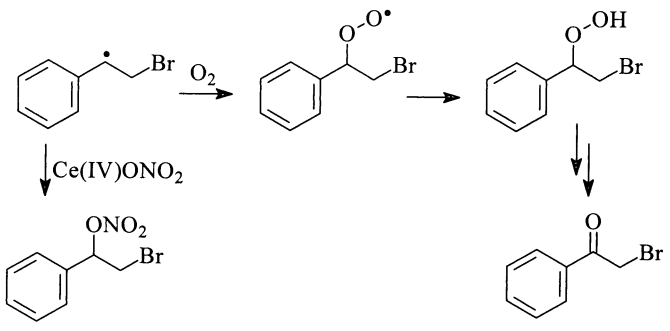
When the reaction was carried out in a deoxygenated atmosphere, as expected, no keto product was formed; instead the nitrato bromide was formed exclusively (Scheme 5).

It is noteworthy that a two phase system consisting of water and dichloromethane is necessary for the reaction to occur. In the absence of a two-phase system, dibromide is not isolated. The success of the reaction may be attributed to the fact that the bromine radicals generated by CAN will be predominantly distributed in the organic phase along with the alkene, thus facilitating the bromination, whereas the oxidant will remain in the aqueous phase; its limited contact with the substrate will minimize the possibility of unwanted side reactions.

3. Mechanistic consideration

Although the mechanistic details of the reactions are far from clear, a rationalization can be made as follows. There is enough circumstantial evidence to suggest that bromide ion can be oxidized to bromine radical by CAN. A comparison of the oxidation/reduction potential of Br^-/Br and Ce(IV)/Ce(III) systems (1.6 for Ce(III)/Ce(IV) and 1.03 V for Br/Br^-) also lends credence to this postulate. Therefore it is reasonable to assume that the bromination reported herein proceeds via a mechanistic pathway involving bromine radical. Conceivably, bromine radical generated by the oxidation of bromide ions can add to the alkene to give a secondary radical. The latter can either undergo oxidation to produce the cation, which on attack by another bromide ion can give the product; or the benzylic radical can be trapped by a bromine radical itself. A third possibility that needs to be considered is the reaction of the secondary radical with molecular bromine, that may be formed by the radical combination, leading to the dibromide.

The formation of the nitrato bromide and/or the phenacyl bromide in methanol and in acetonitrile (Schemes 4 and 5) can also be explained by invoking the transformations of the benzylic radical. The benzylic radical can give rise to the nitrato bromide by ligand transfer or it can be trapped by molecular oxygen producing a peroxy radical, which is



Scheme 6.

further transformed to the hydroperoxide. The hydroperoxide can undergo fragmentation giving the keto bromide.

The exclusive formation of the nitrato bromide in a deoxygenated atmosphere lends support to the postulate that the genesis of the keto product involves the incorporation of molecular oxygen. A schematic representation of the mechanistic pathway is given below. (Scheme 6).

It may be pointed out that a mechanistic postulate involving the intermediacy of bromine radical may be preferred over the one involving the bromonium ion proposed by Asakura et al.[18] Indirect support for a radical mechanism is rendered by the lack of solvent incorporation, in the case of reactions carried out in methanol and acetonitrile. A cationic species resulting from the addition of bromonium ion is likely to be quenched by the solvent under these conditions.

4. Conclusion

In conclusion, we have encountered an efficient route to the synthesis of 1,2-dibromides in a two-phase system. Evidently, the present procedure offers a mild and experimentally simple alternative to the one using bromine, which is toxic, corrosive and expensive. In addition, it appears that the new combination of reagents will find application in the chemoselective bromination of multifunctional compounds. Since the solvent plays an important role in these reactions, suitable selection of the solvent leads to the product of choice. It may be emphasized that, by using the combination of potassium bromide and CAN it is possible to convert styrene into a variety of products such as dibromoalkane, phenacyl bromide and the nitratobromide.

5. Experimental

5.1. General methods

^{1}H and ^{13}C NMR spectra were recorded at 300 MHz NMR instrument. Chemical shifts are reported relative to TMS (^{1}H) and $CDCl_3$ (^{13}C) as the internal standards. Mass spectra were recorded under EI/HRMS. Column chromatography was performed on silica (100–200 mesh). All the solvents were distilled prior to use. Alkenes were purchased and or prepared. The CAN was purchased from Aldrich Co. and was used without further purification.

5.2. General procedure for the preparation of 1,2-dibromide 2[13]

To a solution of styrene (104 mg, 1 mmol) in dichloromethane (10 mL) was added KBr (250 mg, 2.2 mmol) and a solution of CAN (1.26 g, 2.3 mmol) in water (10 mL) at room temperature and stirred. After completion of the reaction, the dichloromethane layer was separated washed with brine and dried over sodium sulfate. The solvent was removed and the residue was crystallized from dichloromethane–hexane mixture to afford white crystals (240 mg, 91%), mp 74–76°C, data consistent with the literature.

5.2.1. 1,2-Dibromo-1-(4-methyl)-phenyl ethane 4. 4-Methylstyrene (236 mg, 2 mmol) on treatment with potassium bromide (500 mg, 4.2 mmol) and CAN (2.56 g, 4.6 mmol) in a two phase system of water and dichloromethane afforded (372 mg, 67%) the dibromide **4** as viscous liquid. IR (neat): 1613, 1512, 1438, 1135, 818 cm^{-1}; ^{1}H NMR: 7.25 (d, 2H, Ar*H*, *J*=7.8 Hz), 7.16–7.13 (d, 2H, Ar*H*, *J*=7.8 Hz), 5.09 (dd, 1H, C*H*Br, *J*=5.5, 10.4 Hz), 4.05–3.95 (m, 2H, CH_2Br), 2.35 (s, 3H, CH_3); ^{13}C NMR: 138.94, 135. 57, 129.43, 127.45, 50.84, 34.86, 21.22; HRMS calcd for $C_9H_{10}Br_2$, 275.9149. Found (M^+) 275.9161, (M^++4) 279.9130.

5.2.2. 1,2-Dibromo-1-(4-chloro)-phenyl ethane 6. 4-Chlorostyrene (138 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (254 mg, 85%) of the dibromide as low melting, pale yellow solid. IR (neat) ν_{max}: 1484, 1091, 1023, 890 cm^{-1}.^{1}H NMR: 7.30 (s, 4H, Ar*H*), 5.08–5.03 (m, 1H, C*H*Br), 4.03–3.87 (m, 2H, CH_2Br); ^{13}C NMR: 137.02, 134.86, 128. 99, 128.96, 49.44, 34.57; HRMS calcd for $C_8H_7Br_2Cl_2$, 295.8603. Found (M^+) 295.8612, (M^++4) 299.8588.

5.2.3. 1,2-Dibromo-1-phenyl propane (8) (mixture of isomers).[8] β-Methylstyrene (118 mg,1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (250 mg, 90%) of the dibromide as a viscous liquid.

5.2.4. 1,2-Dibromo-1-naphthyl ethane 10. Vinylnaphthalene (154 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (298 mg, 95%) of the dibromide as colorless crystals, recrystallized from dichloromethane–hexane mixture, mp 56–58°C; IR (neat) ν_{max}: 1452, 1371, 1141, 996, 761 cm^{-1}; ^{1}H NMR: 7.88–7.81 (m, 4H, Ar*H*), 7.51–7.48 (m, 3H, Ar*H*), 5.30 (dd, 1H, C*H*Br, *J*=7, 9.3 Hz), 4.14–4.08 (m, 2H, CH_2Br); ^{13}C NMR: 135.74, 133.59, 132.98, 129.11, 128.25, 127.83, 127.48, 126.90, 126,69, 124.41, 51.29, 34. 72; HRMS calcd for $C_{12}H_{10}Br_2$, 311.9149. Found (M^+) 311.9134, (M^++4) 315.9096.

5.2.5. 1,2-Dibromo cyclohexane 12. Cyclohexene (410 mg, 5 mmol) on treatment with potassium bromide (1.0 g, 10.1 mmol) and CAN (6.3 g, 11.5 mmol) in a two phase system of water and dichloromethane afforded (786 mg, 65%) of the dibromide as a viscous liquid.[12]

5.2.6. 1,2-Dibromo-3-phenyl propane 14. Allyl benzene (118 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (180 mg, 65%) of the dibromide as colorless oil. IR (neat) ν_{max}: 2995, 1809, 1600, 1494, 1580, 1445 cm^{-1}; ^{1}H NMR: 7.33–7.27 (m, 5H, Ar*H*), 4.36–4.30 (m, 1H, CH_2Br), 3.83–3.78 (m, 1H, CH_2Br), 3.63–3.45(m, 3H), 3.11 (dd, 1H, *J*=7.7, 14.4 Hz; ^{13}C NMR: 136.74, 129.52, 128.49,127. 20, 52.24, 41.92, 35.89; HRMS calcd for $C_9H_{10}Br_2$, 275. 9149. Found (M^+) 275.9152, (M^++4) 279.9123.

5.2.7. 1,2-Dibromo octane 16.[12] 1-Octene (500 mg, 4.5 mmol) on treatment with potassium bromide (1.1 g, 9.3 mmol) and CAN (5.7 g, 10.35 mmol) in a two phase system of water and dichloromethane afforded (624 mg, 51%) of the dibromide as viscous liquid.[12]

5.2.8. 1,2-Dibromo hexane 18.[12] 1-Hexene (170 mg, 2 mmol) on treatment with potassium bromide (500 mg, 4.2 mmol) and CAN (2.5 g, 4.6 mmol) in a two phase system of water and dichloromethane afforded 82% (450 mg) of the dibromide as colorless viscous liquid.

5.2.9. 2,3-Dibromo-3-phenylmethyl propanoate 20.[15] Methyl cinnamate (162 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (250 mg, 78%) of the dibromide as colorless crystals, recrystallized from dichloromethane–hexane mixture, mp 114–116°C.

5.2.10. 2,3-Dibromo-3-(3,4-dimethoxy)-phenylethyl propanoate 22. Cinnamyl ester (236 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (316 mg, 80%) of the dibromide as light yellow crystals, recrystallized from dichloromethane–hexane mixture, mp 102–104°C; IR (KBr) ν_{max}: 1738, 1600, 1513, 1463, 1369, 1331, 849, 801 cm^{-1}.^{1}H NMR 6.99–6.81 (m, 3H, Ar*H*), 5.31 (d, 1H, C*H*Br *J*=11.7 Hz), 4.79 (d, 1H, C*H*Br, *J*=11.7 Hz), 4.36 (q, 2H, OCH_2, *J*=7 Hz), 3.92 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 1.39 (t, 3H, CH_3, *J*=7.1 Hz); ^{13}C NMR: 167.70, 149.91, 149.27, 129.98, 120.98, 110.89, 110.69, 62.53, 55.95, 55.86, 51.57, 47.37, 13.98; HRMS calcd for $C_{13}H_{16}Br_2O_4$; 392.933. Found (M^+) 392.9325.

5.2.11. 3,4-Dibromo 4-phenyl butan-2 one 24.[13] Benzylidene acetone (146 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.3 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (252 mg, 81%) of the dibromide as colorless crystals, recrystallized from dichloromethane–hexane mixture, mp 118–120°C.

5.2.12. 2,3-Dibromo-1,3-diphenylpropan-1-one 26.[6] Chalcone (208 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (351 mg, 95%) of the dibromide as colorless crystals, recrystallized from dichloromethane–hexane mixture, mp 156–158°C.

5.2.13. (2,3-Dibromo)allyl(4-acetoxy)phenyl ether 28. Allyl phenyl ether (174 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (250 mg, 75%) of the dibromide as colorless crystals, recrystallized from dichloromethane–hexane mixture, mp 44–46°C; IR (neat) ν_{max}: 1680, 1604, 1506, 1363, 1251, 1174, 831, 581 cm^{-1} ^{1}H NMR: 7.92 (d, 2H Ar*H*, *J*=8.2 Hz), 6.95 (d, 2H, Ar*H*, *J*=8.2 Hz), 4.43 (broad triplet, 3H, OCH_2, C*H*Br), 3.89 (d, 2H, CH_2Br), 2.54 (s, 3H, CH_3). ^{13}C NMR: 195.97, 161.58, 131.09, 130.52, 114.33, 69.04, 46.99, 32.99, 26.24.HRMS calcd for $C_{11}H_{12}O_2Br_2$, 333.9204. Found (M^+) 333.9194, (M^++4) 337.9173.

5.2.14. (2,3-Dibromo)allyl(2-acetoxy)phenyl ether 30. Allylphenyl ether (174 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (267 mg, 79%) of the dibromide as colorless viscous liquid IR (neat) ν_{max}: 1676, 1595, 1483, 1452, 1290, 1159 cm^{-1}.^{1}H NMR: 7.73 (d, 1H, Ar*H* *J*=7.5 Hz), 7.43 (m, 1H, Ar*H*), 7.03 (t, 1H, ArH *J*=7.4 Hz), 6.93 (d, 1H, Ar*H*, *J*=8.3 Hz), 4.49 (broad triplet, 3H, OCH_2, C*H*Br), 3.90 (broad triplet, 2H, CH_2), 2.67 (s, 3H, CH_3);^{13}C NMR: 190.70, 156.92, 133.52, 130.69, 128.70, 121.57, 112.51, 69.71, 46.98, 32.15, 32.06; HRMS calcd for $C_{11}H_{12}Br_2O_2$; 333.9204. Found (M^+) 333.9200, (M^++4) 337.9176.

5.2.15. 1,2-Dibromo-1-phenyl ethene 32a.[15] Phenylacetylene (102 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (210 mg, 80%) of the dibromoethene as a 2:3 mixture of *E* and *Z* isomers.

5.2.16. 1,2-Dibromo-1,2-diphenylethene 32b.[15] Diphenylacetylene (178 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.3 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (317 mg, 94%) of the dibromoethene as mixture of *E* and *Z* isomers.

5.2.17. 1,2-Dibromo-1-hex-1-ene 32c.[15] 1-Hexyne (82 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (194 mg, 79%) of the dibromoethene as a 2:1 mixture of *E* and *Z* isomers.

5.2.18. 3,4-Dibromo-4-octyne 32d.[15] 4-Octyne (110 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in a two phase system of water and dichloromethane afforded (202 mg, 75%) of the dibromide as colorless liquid.

5.2.19. 1-Nitrato-1-phenyl-2-bromoethane (34) and 1-bromoacetophenone (33). Styrene (104 mg, 1 mmol) on treatment with potassium bromide (250 mg, 2.1 mmol) and CAN (1.26 g, 2.3 mmol) in the solvent (methanol, acetonitrile, acetic acid–acetonitrile mixture or *tert*-butanol) for 1–6 h, after work up and purification afforded the nitrato bromide **34** as pale yellow viscous liquid and phenacylbromide **33** as colorless solid. 1-Nitrato-1-phenyl-2-bromoethane (**34**) IR (neat) ν_{max}: 1645, 1489, 1452, 1278, 1209, 855 693 cm^{-1}; ^{1}H NMR: 7.39 (brs, 5H, Ar*H*), 5.97 (dd, 1H, C*H*ONO_2, *J*=8.3 Hz, 5.1 Hz), 3.69–3.53 (m, 2H, CH_2Br); ^{13}C NMR: 135.21, 129.82, 129.07, 126.60, 83.82, 30.41; HRMS calcd for $C_8H_8BrNO_3$; (M^+), 244.9687. Found 244.9694, (M^++2) 246.9662. 1-Bromo acetopheneone (**33**)[19] mp 46–48°C; IR (neat) ν_{max}: 1682, 1451, 1276, 1195, 1108, 997, 752 cm^{-1}; ^{1}H NMR: 8.01 (t, 2H, Ar*H*, *J*= 7.2 Hz),7.69 (t, 2H, Ar*H* *J*=7.3 Hz), 7.61 (d, Ar*H* *J*=7.6 Hz), 4.44 (s, 2H, CH_2).

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