



A mild and efficient method for oxidative halodecarboxylation of α,β -unsaturated aromatic acids using lithium bromide/chloride and ceric ammonium nitrate

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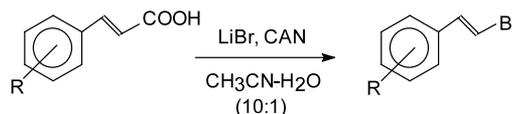
Abstract—A mild and efficient ecofriendly method for the halodecarboxylation of α,β -unsaturated aromatic acids has been developed by using lithium bromide/chloride and ceric ammonium nitrate in acetonitrile–water at room temperature to afford the vinyl halides in moderate to good yields. © 2001 Elsevier Science Ltd. All rights reserved.

The decarboxylation of organic carboxylic acids accompanied by a simultaneous replacement by a halogen under radical conditions is an extremely useful and selective reaction in organic chemistry for the synthesis of halogenated organic substances. The original method for oxidative halodecarboxylation, known as the Hunsdiecker reaction, is the reaction of a silver salt of a carboxylic acid with mainly bromine as the halogen.¹ The efficacy of the reaction has been improved by several groups to include carboxylates of mercury,² thallium,³ lead,⁴ and manganese⁵ besides the original silver of Hunsdiecker. In spite of that, the classical Hunsdiecker reactions have some limitations e.g. (i) the reaction of *trans* and *cis* cinnamic acids give β -bromostyrene in a very low yield,⁶ (ii) generally, a high temperature is required for the reaction (iii) the use of toxic or hazardous reagents like molecular bromine and salts of mercury, thallium, lead and silver.

Later, classical Hunsdiecker reactions have been modified by using NBS/iodosyl benzene,⁷ NBS/lithium acetate,⁸ NBS/tetrabutylammonium trifluoroacetate,⁹ and bis(collidine) halogen(I)hexafluorophosphate.¹⁰ Very recently, microwave induced Hunsdiecker reactions using *N*-halosuccinimide/catalytic amount of lithium acetate¹¹ and sodium halide/oxone¹² have been reported. Although, most of these methods are quite satisfactory, the use of expensive and complex reagents, large amounts of solvent and prolonged reaction times

demand some mild and efficient alternative reagents for the Hunsdiecker reaction.

Lanthanide salts have been used as shift reagents and reagents for organic synthesis.¹³ Ceric ammonium nitrate (CAN) is one such reagent, which has been used extensively for functional group transformations in organic synthesis. The strong oxidising power of the ceric ion has been recognised for many decades. However, its synthetic utility to organic chemistry has only been explored recently.¹⁴ Asakura¹⁵ has demonstrated that CAN can be efficiently used as a one electron oxidant to generate electrophilic bromine from the metal salts. In continuation of our efforts¹⁶ to explore CAN as a one electron oxidant, we report here a simple and efficient methodology for the halodecarboxylation of α,β -unsaturated aromatic acids using LiBr or LiCl and CAN, at room temperature to afford the vinyl halides (Scheme 1). Thus, a series of *trans*- α,β -unsaturated aromatic acids were treated with LiX (X=Cl or Br) and CAN in acetonitrile–water (10:1) at room temperature to afford *trans*- β -halostyrenes.¹⁷ The results are summarised in Table 1. It is noteworthy that the amount of water in the solvent had a remarkable effect on the yield. An increase of water content in the solvent resulted in an increase in the yield of β -



Scheme 1.

Keywords: halodecarboxylation; lithium bromide; ceric ammonium nitrate; α,β -unsaturated aromatic acids.

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Table 1. Halodecarboxylation of α,β -unsaturated aromatic acids with CAN and LiBr/LiCl

Entry	Starting material	Product	Time (h)	Yield (%) ^a
1			3	60
2			1	81
			3	67
3			0.75	85
			1.5	64
4			1.5	85
			3	63
5			3	42
6			1	57
			3	43

^aYields refer to chromatographically pure isolated yield.

halostyrene¹² and we obtained the maximum yield using a solvent to water ratio of 10:1. Moderate to good yields of the corresponding halides were obtained and it was observed that electron donating substituents in the aromatic ring accelerated the reaction.

In conclusion, we have developed a simple, efficient and environmentally friendly methodology for the halodecarboxylation of α,β -unsaturated aromatic acids using lithium bromide/chloride and ceric ammonium nitrate at room temperature.

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References

1. Wilson, C. V. *Org. React.* **1957**, *9*, 332.
2. Cristol, S. J.; Firth, W. C. *J. Org. Chem.* **1961**, *26*, 280.
3. McKillop, A.; Bromley, D.; Taylor, E. C. *J. Org. Chem.* **1969**, *34*, 1172.
4. (a) Barton, D. H. R.; Faro, H. P.; Serebryakov, E. P.; Woolsey, N. F. *J. Chem. Soc.* **1965**, 2438; (b) Sheldon, R. A.; Kochi, J. K. *Org. React.* **1972**, *19*, 275.
5. Chowdhury, S.; Roy, S. *Tetrahedron Lett.* **1996**, *37*, 2623.
6. Johnson, R. G.; Ingham, R. K. *Chem. Rev.* **1956**, *56*, 219.

7. Graven, A.; Jorgensen, K. A.; Dahl, S.; Stanczak, A. *J. Org. Chem.* **1994**, *59*, 3543.
8. Chowdhury, S.; Roy, S. *J. Org. Chem.* **1997**, *62*, 199.
9. Naskar, D.; Roy, S. *Tetrahedron Lett.* **2000**, *56*, 1369.
10. (a) Homsí, F.; Rousseau, G. *Tetrahedron Lett.* **1999**, *64*, 81; (b) Homsí, F.; Rousseau, G. *J. Org. Chem.* **1999**, *64*, 81.
11. Kuang, C.; Senboku, H.; Tokuda, M. *Synlett* **2000**, 1439.
12. You, H.-W.; Lee, K. J. *Synlett* **2001**, 105.
13. Long, J. R. *Aldrichimica Acta* **1985**, *18*, 87 and references cited therein.
14. (a) Ho, T. L. *Synthesis* **1973**, 347; (b) Ho, T. L. In *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J.; Jonge, R.-H. I., Eds.; Plenum Press: New York, 1986.
15. (a) Asakura, J.; Robins, M. J. *Tetrahedron Lett.* **1988**, *29*, 2855; (b) Asakura, J.; Robinson, M. J. *J. Org. Chem.* **1990**, 4928.
16. Roy, S. C.; Guin, C.; Rana, K. K.; Maiti, G. *Synlett* **2001**, 226.
17. General procedure: To a magnetically stirred solution of the cinnamic acid derivative (1.68 mmol), LiBr or LiCl (3.7 mmol) in acetonitrile–water (7.7 ml, 10:1) a solution of ceric ammonium nitrate (3.5 mmol) in acetonitrile (10 ml) was added dropwise at room temperature under nitrogen. After completion of the reaction (monitored by TLC) the reaction mixture was diluted with ether (25 mL). The organic layer was washed successively with saturated aqueous NaHCO₃ solution (3×10 ml), water (2×10 ml), brine (3×10 ml) and then dried (Na₂SO₄). Volatiles were removed under reduced pressure and the residue was purified by chromatography over Al₂O₃ (2% ethylacetate in petroleum ether) to furnish the pure vinyl halides.