Halodecarboxylation of *a*,β-Unsaturated Carboxylic Acids bearing Aryl and Styrenyl Group at β-Carbon with Oxone® and Sodium Halide

Ho-Woong You, Kee-Jung Lee*

Department of Industrial Chemistry, Hanyang University, Seoul 133-791, South Korea
Fax +82-2-2298-4101; E-mail: leekj@email.hanyang.ac.kr

Received 21 October 2000

Abstract: Reaction of *a*,β-unsaturated carboxylic acid bearing aryl and styrenyl group at β-carbon with Oxone® and sodium halide in aqueous acetonitrile afforded the corresponding haloalkenes.

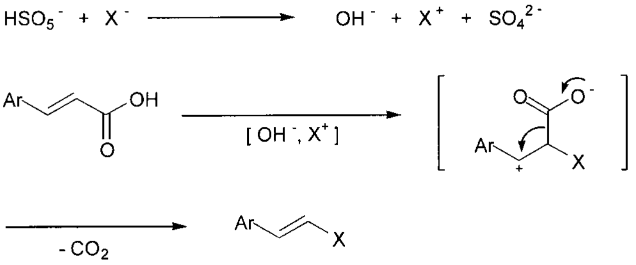
Key words: halodecarboxylation, Hunsdiecker reaction, Oxone, sodium halide, α,β-unsaturated aromatic carboxylic acid

The halodecarboxylation of metal carboxylates with molecular bromine, commonly known as the Hunsdiecker reaction, is an extremely useful and selective procedure for the syntheses of halogenated organic substances.[1] The efficacy of the reaction has been improvised by several groups to include carboxylates of mercury,[2] thallium,[3] lead,[4] and manganese[5] besides the original silver of Hunsdiecker. In addition an oxidative decarboxylation protocols using iodosylbenzene/*N*-bromosuccinimide (NBS),[6] lithium acetate/NBS,[7] and tetrabutylammonium trifluoroacetate/*N*-halosuccinimides[8] are reported. This paper describes the halodecarboxylation of various α,β-unsaturated carboxylic acids bearing aryl and styrenyl group at β-carbon with Oxone® and sodium halide in aqueous acetonitrile under the mild conditions.

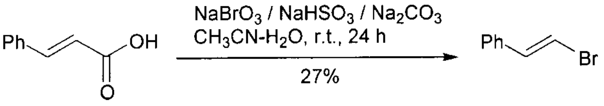
Recent reports have dealt with the use of potassium hydrogen persulfate ($KHSO_5$), which is commercially available as Oxone®, can be used for the oxidation of alkenes,[9] arenes,[10] amines,[11] imines,[12] sulfides,[13] selenides,[14] α-amino acids,[15] acetals,[16] and the carbonyl regeneration from thioacetals,[17] oximes[18] and nitroalkanes.[19] Moreover, the use of Oxone® and aqueous sodium halide was conducted as a convenient halogenating reagent to achieve oxidation of α,β-enones,[20] bromination of pyrimidines,[21] and halogenation of toluene.[9]

Thus reaction of cinnamic acid (3 mmol) with sodium bromide (9 mmol), sodium carbonate (3 mmol) and Oxone® (3 mmol) in 50 mL of acetonitrile/water (3:2 v/v) at room temperature for 3 h furnished after work-up, β-bromostyrene in 88% isolated yield. Analogous chlorodecarboxylation using sodium chloride afforded β-chlorostyrene in 84% yield, however, iododecarboxylation did not proceed at all. On the other hand, electron-rich *para*-methoxycinnamic acid afforded iododecarboxylation product, *para*-methoxy-β-iodostyrene in 45% yield. The methodology was extended to bromo-, chloro- and iododecarboxylation of various α,β-unsaturated aromatic carboxylic acids with sodium halide with Oxone®. The moderate to excellent yields of corresponding halides except iodides were obtained and generally acids bearing electron-donating substituents were particularly reactive compared to those having electron-withdrawing groups (Table).[22] Also these reactions showed the good degree of stereospecificity, wherein (*E*)-acids gave rise to corresponding (*E*)-haloalkenes.

A plausible mechanism of the halodecarboxylation is shown in Scheme 1 based on the literature. The oxidation of halide ion by peroxymonosulfate ion would give the hypohalite ion[23] and subsequent halogenation at carbon-carbon double bond and followed by decarboxylation afford β-halostyrene.[6,8,24] Experimental evidence for this mechanism might be explained by the production of β-bromostyrene (27% yield) from the reaction of cinnamic acid with hypobromous acid (HOBr) in situ generation from sodium bromate and sodium hydrogensulfite mixture ($NaBrO_3/NaHSO_3$) (Scheme 2).[25]



Scheme 1



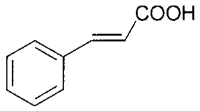
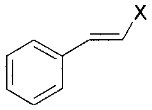
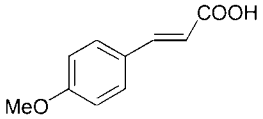
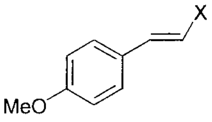
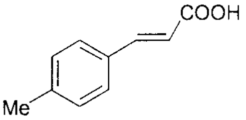
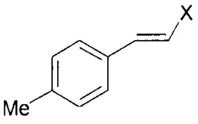
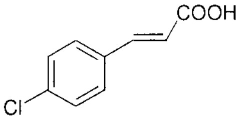
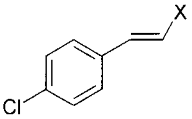
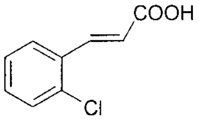
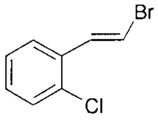
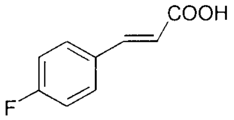
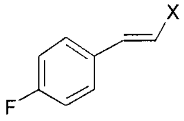
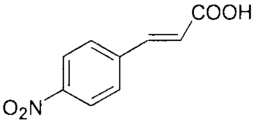
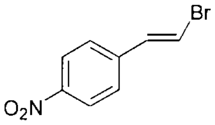
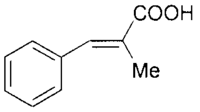
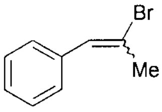
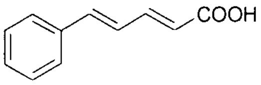
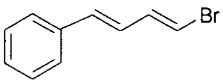
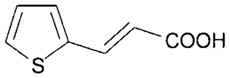
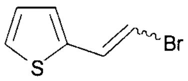
Scheme 2

In summary, we have shown that facile halodecarboxylation of α,β-unsaturated carboxylic acids can be carried out using a mixture of Oxone® and sodium halide, thus further widening the scope of the Hunsdiecker reaction. The described procedure is safe and economically and environmentally advantageous over reported methods.

Acknowledgement

This work was supported by the research fund of Hanyang University (HY-2000).

Table Halodecarboxylation of α,β-Unsaturated Carboxylic Acids bearing Aryl and Styrenyl Group at β-Carbon with Oxone® and Sodium Halide

Entry	Acid	Product	X	Pdt.No.	Reaction Time (h)	Yield (%)
1			Br Cl I	**1a** **1b** **1c**	3 12 24	88 84 0
2			Br Cl I	**2a** **2b** **2c**	2 12 12	97 88 45
3			Br Cl I	**3a** **3b** **3c**	1 12 24	93 82 12
4			Br Cl I	**4a** **4b** **4c**	1 12 24	85 73 0
5			Br	**5a**	24	40
6			Br Cl I	**6a** **6b** **6c**	3 12 24	85 80 0
7			Br	**7a**	24	48[a]
8			Br	**8a**	7	64[b]
9			Br	**9a**	24	59
10			Br	**10a**	0.5	93[c]

[a] 3 Eq. of Oxone® was used at reflux temperature. [b] E:Z = 75:25 (vide 300 MHz ^{1}H NMR). [c] E:Z = 70:30 (vide 300 MHz ^{1}H NMR).

References and Notes

(1) (a) Hunsdiecker, H. C. *Chem. Ber.* **1942**, *75*, 291. (b) Crich, D. *In Comprehensive Organic Synthesis*; Trost, B. M., Steven, V. L., Eds.; Pergamon: Oxford, 1991; Vol. 7, p 717. (c) Sheldon, R. A.; Kochi, J. K. *Org. React.* (*N. Y.*) **1972**, *19*, 326.

(2) Cristol, S. J.; Firth, W. C., Jr. *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. (N. Y.)* **1972**, *19*, 279.

(5) Chowdhury, S.; Roy, S. *Tetrahedron Lett.* **1996**, *37*, 2623.

(6) Graven, A.; Jorgensen, K. A.; Dahl, S.; Stanczak, A. *J. Org. Chem.* **1994**, *59*, 3543.

(7) Chowdhury, S.; Roy, S. *J. Org. Chem.* **1997**, *62*, 199.

(8) Naskar, D.; Roy, S. *Tetrahedron* **2000**, *56*, 1369.

(9) Kennedy, R. J.; Stock, A. M. *J. Org. Chem.* **1960**, *25*, 1901.

(10) Jeyaraman, R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 2462.

(11) Zabrowski, D. L.; Moormann, A. E.; Beck, K. R. J. *Tetrahedron Lett.* **1988**, *29*, 4501.

(12) Davis, F. A.; Chattopadhyay, S.; Towson, J. C.; Lal, S.; Reddy, T. *J. Org. Chem.* **1988**, *53*, 2087.

(13) Greenhalgh, R. P. *Synlett* **1992**, 235.

(14) Ceccherelli, P.; Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O. *J. Org. Chem.* **1995**, *60*, 8412.

(15) Paradkar, V. M.; Latham, T. B.; Demko, D. M. *Synlett* **1995**, 1059.

(16) Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O. *Synlett* **1999**, 777.

(17) Ceccherelli, P.; Curini, M.; Marcotullio, M. C.; Epifano, F.; Rosati, O. *Synlett* **1996**, 767.

(18) Subhas Bose, D.; Srinivas, P. *Synth. Commun.* **1997**, *27*, 3835.

(19) Ceccherelli, P.; Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O. *Synth. Commun.* **1998**, *28*, 3057.

(20) Dieter, R. K.; Nice, L. E.; Velu, S. E. *Tetrahedron Lett.* **1996**, *37*, 2377.

(21) Ross, S. A.; Burrows, C. J. *Tetrahedron Lett.* **1997**, *38*, 2805.

(22) *General procedure for the halodecarboxylation of a,β-unsaturated aromatic carboxylic acids:* Sodium halide (9 mmol), and sodium carbonate (3 mmol, 0.32 g), was added to a stirred solution of carboxylic acid (3 mmol) in 50 mL of CH_3CN-H_2O (3:2 v/v), and then followed by the dropwise addition of Oxone® (3 mmol, 1.84 g), in 20 mL of H_2O. Reactions were continuously monitored by thin-layer chromatography and stirred at r.t. for generally 1 h to 24 h. The reaction mixture was quenched with aqueous sodium thiosulfate, and extracted with Et_2O (3×50 mL). The combined organic layers were washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was chromatographed on a silica gel column and eluted with hexane-ethyl acetate 20:1 to give the products. The spectral and analytical data of products are as follows: **1a**, **1b**, **2a**, **2b**, **2c**, **3a**, **3b**, **3c**, **4a**, **4b**, **8a**, and **9a**. Lit.[6, 7, 8] (300 MHz ^{1}H NMR is identical).

5a: oil. ^{1}H NMR ($CDCl_3$): *δ* 6.80 (d, 1H, *J* = 14.0 Hz), 7.21-7.42 (m, 4H), 7.47 (d, 1H, *J* = 14.0 Hz). Anal. Calcd. for C_8H_6BrCl: C, 44.18; H, 2.78. Found: C, 44.02; H, 2.59.

6a: oil. ^{1}H NMR ($CDCl_3$): *δ* 6.69 (d, 1H, *J* = 14.0 Hz), 6.98-7.29 (m, 5H). Anal. Calcd. for C_8H_6BrF: C, 47.80; H, 3.01. Found: C, 47.58; H, 2.83.

6b: oil. ^{1}H NMR ($CDCl_3$): *δ* 6.56 (d, 1H, *J* = 13.7 Hz), 6.79 (d, 1H, *J* = 13.7 Hz), 6.98-7.28 (m, 4H). Anal. Calcd. for C_8H_6ClF: C, 61.36; H, 3.86. Found: C, 61.12; H, 3.66.

7a: m.p. 158-159° (Lit.[26] 160°). ^{1}H NMR ($CDCl_3$): δ 7.03 (d, 1H, *J* = 14.0 Hz), 7.19 (d, 1H, *J* = 14.0 Hz), 7.45 (d, 2H, *J* = 8.9 Hz), 8.20 (d, 2H, *J* = 8.9 Hz).

10a: oil. (Lit.[27] b.p. 89°/5 Torr.). ^{1}H NMR ($CDCl_3$): δ 6.29 (d, 0.3H, *J* = 7.9 Hz), 6.60 (d, 0.7 H, *J* = 14.0 Hz), 6.94-7.34 (m, 4H).

(23) Montgomery, R. E. *J. Am. Chem. Soc.* **1974**, *96*, 7820.

(24) The Oxidation of cinnamate by the peroxymonosulfate ion in the presence of ketone gave *α*,β-epoxy acid: Gallopo, A. R.; Edwards, J. O. *J. Org. Chem.* **1981**, *46*, 1684.

(25) Kikuchi, D.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **1998**, *63*, 6023.

(26) Trumbull, E. R.; Finn, R. T.; Ibne-Rasa, K. M.; Sauers, C. K. *J. Org. Chem.* **1962**, *27*, 2339.

(27) Rossi, R.; Carpita, A.; Lippolis, V. *Synth. Commun.* **1991**, *21*, 333.

Article Identifier:
1437-2096,E;2001,0,01,0105,0107,ftx,en;Y18000ST.pdf