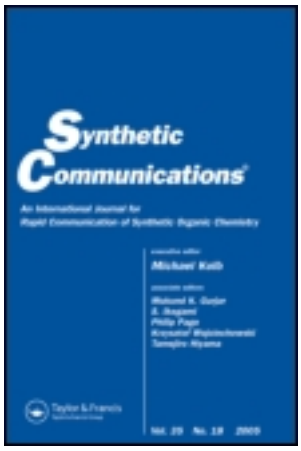


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

BROMODECARBONYLATION AND BROMODECARBOXYLATION OF ELECTRON-RICH BENZALDEHYDES AND BENZOIC ACIDS WITH OXONE® AND SODIUM BROMIDE

Bon-Suk Koo [a], Eun-Hoo Kim [a] & Kee-Jung Lee [b]

[a] Department of Industrial Chemistry, Hanyang University, Seoul, 133-791, Korea

[b] Department of Industrial Chemistry, Hanyang University, Seoul, 133-791, Korea

Version of record first published: 16 Aug 2006

To cite this article: Bon-Suk Koo, Eun-Hoo Kim & Kee-Jung Lee (2002): BROMODECARBONYLATION AND BROMODECARBOXYLATION OF ELECTRON-RICH BENZALDEHYDES AND BENZOIC ACIDS WITH OXONE® AND SODIUM BROMIDE, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:15, 2275-2286

To link to this article: http://dx.doi.org/10.1081/SCC-120005997

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SYNTHETIC COMMUNICATIONS
Vol. 32, No. 15, pp. 2275–2286, 2002

BROMODECARBONYLATION AND BROMODECARBOXYLATION OF ELECTRON-RICH BENZALDEHYDES AND BENZOIC ACIDS WITH OXONE® AND SODIUM BROMIDE

Bon-Suk Koo, Eun-Hoo Kim, and Kee-Jung Lee*

Department of Industrial Chemistry,
Hanyang University, Seoul 133-791, Korea

ABSTRACT

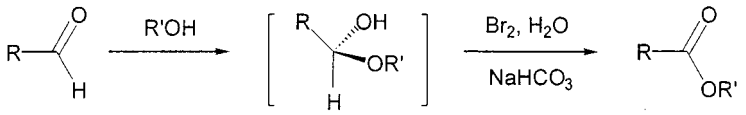
Benzaldehydes and benzoic acids bearing *ortho*- and *para*-electron donating substituents having unshared electron-pair have undergone bromodecarbonylation or bromodecarboxylation on treatment with sodium bromide in the presence of Oxone® in aqueous methanol.

Key Words: Bromodercarbonylation; Bromodecarboxylation; Oxone; Sodium bromide; Electron-rich benzaldehydes; Benzoic acids

Potassium hydrogen persulfate ($KHSO_5$), which is commercially available as Oxone®, can be used for the oxidation of alkenes,[1] arenes,[2]

*Corresponding author. Fax: +82-2-2298-4101; E-mail: leekj@hanyang.ac.kr

DOI: 10.1081/SCC-120005997 0039-7911 (Print); 1532-2432 (Online)

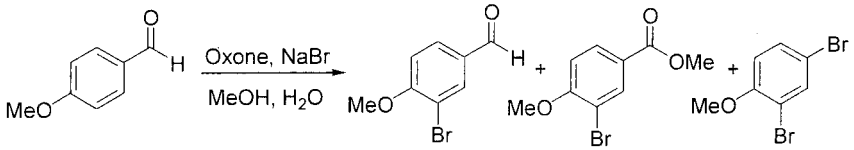


Scheme 1.

amines,[3] imines,[4] sulfides,[5] selenides,[6] α-amino acids,[7] acetals,[8] and the carbonyl regeneration from thioacetals,[9] oximes[10] and nitroalkanes.[11] Recent reports deal with the use of Oxone® and aqueous sodium halides as a convenient halogenating reagent to achieve oxidation of α,β-enones[12] and bromination of pyrimidines.[13] Also, the use of bromine in alcohol has been used to convert aldehydes to esters as a convenient and inexpensive technique,[14] as shown in Scheme 1.

Based on the versatility of Oxone® as an oxidant and on halogen generation from sodium halide, and on the fact that these strongly acidic solutions may provide some advantage for direct conversion of aldehydes into esters, we decided to test Oxone® and sodium bromide on benzaldehydes in aqueous methanol. Our results are compiled in Table 1; yields were determined after isolation. Methyl and ethyl esters were prepared in good to excellent yields, but *iso*-propyl ester was not produced in any quantity (Entries 1 and 2). However, an electron-rich aromatic, *p*-anisaldehyde, underwent competitive attack on the ring, giving 3-bromo-*p*-anisaldehyde **3a** (39%), methyl 3-bromo-*p*-anisate **3b** (5%), and affording, unexpectedly, bromodecarbonylation product, 2,4-dibromoanisole **3c** (38%).[15] In the case of using two equivalents of Oxone®, **3c** was produced in excellent yield (78%) along with **3b** (11%) (Entry 3), as shown in Scheme 2.

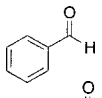
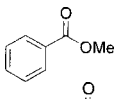
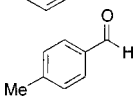
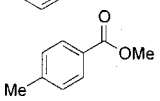
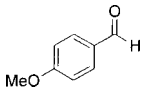
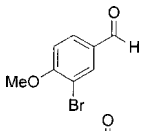
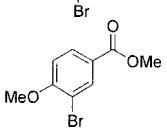
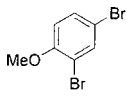
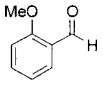
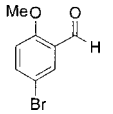
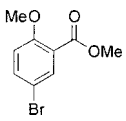
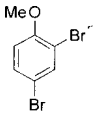
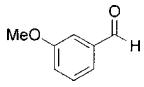
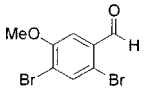
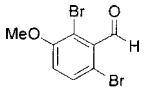
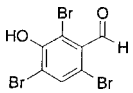
Analogous bromodecarbonylation of *o*-anisaldehyde, using two equivalents of Oxone®, afforded 2,4-dibromoanisole **3c** (15%) and the



1 eq.	39%	5%	38%
2 eq.		11%	78%

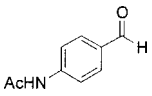
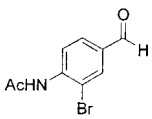
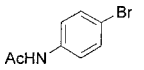
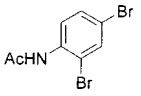
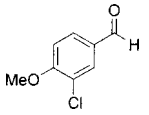
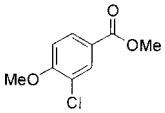
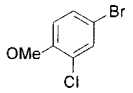
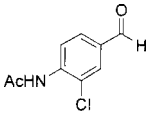
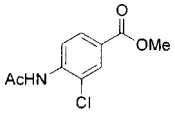
Scheme 2.

Table 1. Reaction of Benzaldehydes with Oxone® and Sodium Bromide

Entry	Substrate	Time (h)	Product/No.	% Yield[a]
1[b]		24	 **1a**	(71)
2		4	 **2**	(90)
3		4	 **3a**	39 (0)
			 **3b**	5 (11)
			 **3c**	38 (78)
4		24	 **4a**	72 (5)
			 **4b**	0 (15)
			 **3c**	0 (15)
5		24	 **5a**	73 (49)
			 **5b**	0 (10)
			 **5c**	0 (14)

(*continued*)

Table 1. Continued

Entry	Substrate	Time (h)	Product/No.		% Yield[a]
6		4		**6a**	27 (0)
				**6b**	37 (0)
				**6c**	14 (65)
7		24		**7a**	(22)
				**7b**	(37)
8		4		**8**	(95)

[a]Yields were based on isolated products purified by column chromatography using 1 eq. of Oxone®. Parentheses values were obtained using 2 eq. of Oxone®.
[b]Ethyl benzoate (**1b**) (65%) was obtained using EtOH instead of MeOH, but *iso*-propyl benzoate was not produced in *iso*-PrOH.

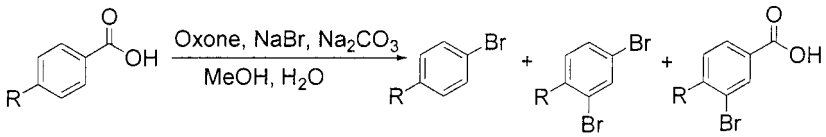
ring bromination products, 5-bromo-*o*-anisaldehyde **4a** (5%) and methyl 5-bromo-*o*-anisate **4b** (15%) (Entry 4). However, *m*-anisaldehyde gave only ring bromination aldehydes **5a** (49%) and **5b** (10%) along with a demethylation product, 2,4,6-tribromo-3-hydroxybenzaldehyde **5c** (14%), using two equivalents of Oxone® (Entry 5). To further investigate the generality of our protocol, various aldehydes were chosen. 4-Acetamidobenzaldehyde afforded bromodecarbonylation products, 4-bromoacetanilide **6b** (37%), 2,4-dibromoacetanilide **6c** (14%) and a simple ring bromination product, 3-bromo-4-acetamidobenzaldehyde **6a** (27%). But **6c** (65%) was produced using two equivalents of Oxone® (Entry 6). Moreover, a salient feature of these reactions is the possibility of introducing two different halo-

gens into the aromatic ring, selectively (Entry 7). But, in the case of 4-acetamido-3-chlorobenzaldehyde, methyl 4-acetamido-3-chlorobenzoate **8** (95%) was obtained, exclusively (Entry 8).

Electron-deficient aromatic aldehydes have been shown to undergo oxidation with Oxone® to give acids. However, electron-rich aromatic aldehydes such as *p*-anisaldehyde, are converted to the Dakin product, *p*-methoxyphenol.[16] The major question that warranted further investigation in the present study is: "what triggers the elimination of the aldehyde group?"[17]

To elucidate the possible pathway for the formation of the bromodecarbonylation product, we next subjected various substituted benzoic acids to our reaction conditions (Table 2). For example, the reaction of electron-rich aromatic *p*-anisic acid with Oxone®/NaBr/Na_2CO_3 in aqueous methanol at r.t. afforded the bromodecarboxylation product 4-bromoanisole **9b** (58%) and the ring bromination product 3-bromo-*p*-anisic acid **9a** (13%) (Entry 1). Similarly, 4-acetamidobenzoic acid gave 4-bromoacetanilide **6b** (56%), 2,4-dibromoacetanilide **6c** (7%) and 4-acetamido-3-bromobenzoic acid **10a** (23%), respectively (Entry 2). Using two equivalents of Oxone®, we obtained 2,4-dibromoanisole **3c** (91%) and 2,4-dibromoacetanilide **6c** (65%) from *p*-anisic acid and 4-acetamidobenzoic acid, respectively (Entries 1 and 2) as shown in Scheme 3.

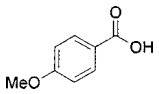
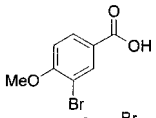
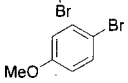
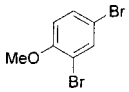
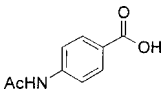
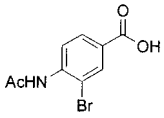
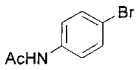
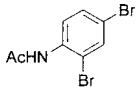
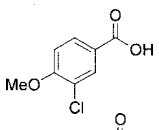
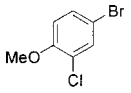
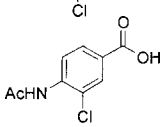
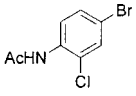
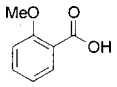
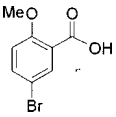
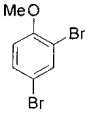
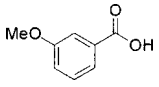
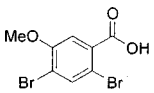
This modified Hunsdiecker reaction[18] was further extended to the analogous benzoic acids such as 3-chloro-*p*-anisic acid and 4-acetamido-3-chlorobenzoic acid, which afforded the corresponding bromides **7b** (72%) and **11** (43%), respectively (Entries 3 and 4). This is another valuable reaction that introduces two different halogens into the aromatic ring, selectively.



R = OMe;	1 eq.	58%		13%
	2 eq.		91%	
R = NHAc;	1 eq.	56%	7%	23%
	2 eq.		65%	

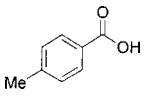
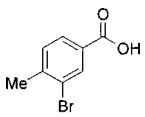
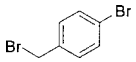
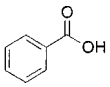
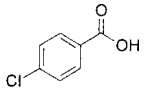
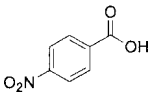
Scheme 3.

Table 2. Reaction of Benzoic Acids with Oxone® and Sodium Bromide

Entry	Substrate	Time (h)	Product/No.	% Yield[a]
1		24	 **9a**	13 (0)
			 **9b**	58 (0)
			 **3c**	0 (91)
2		24	 **10a**	23 (0)
			 **6b**	56 (0)
			 **6c**	7 (65)
3		24	 **7b**	(72)
4		24	 **11**	(43)
5		24	 **12**	65 (25)
			 **3c**	30 (68)
6		24	 **13**	75 (75)

(*continued*)

Table 2. Continued

Entry	Substrate	Time (h)	Product/No.		% Yield[a]
7		24		**14a**	(71)
				**14b**	(8)
8		24	[b]		
9		24	[b]		
10		24	[b]		

[a]Yields were based on isolated products purified by column chromatography using 1 eq. of Oxone®. Parentheses values were obtained using 2 eq. of Oxone®.
[b]No reaction and starting acid was recovered.

To gain further insight, various independent experiments have been conducted in the present study, the results of which are presented below; (a) acids bearing *ortho*- and *para*-electron donating substituents having unshared electron-pair are particularly reactive (Table 2, Entries 1–3 and 5) compared with those having electron withdrawing groups (Table 2, Entries 9 and 10); (b) acids bearing *meta*-electron donating substituents give only ring bromination products (Table 2, Entry 6); (c) electron-rich aromatics such as *p*-toluic acid give mainly ring bromination products, 3-bromo-*p*-toluic acid **14a** (71%) and bromodecarboxylation/concurrent with the side chain bromination product,[1a] 4-bromobenzyl bromide **14b** (8%) (Table 2, Entry 7).

We have shown in the present study that facile bromodecarbonylation[19] and bromodecarboxylation[19] of benzaldehydes and benzoic acids can be carried out using a mixture of Oxone® and NaBr, thus further widening the scope of the Hunsdiecker reaction. The procedure described here is safe, economical and environmentally sound compared with other reported methods. In further studies, we hope to elaborate

the mechanism of reaction and provide examples of this modified Hunsdiecker reaction on substrates other than benzaldehydes and benzoic acids.

EXPERIMENTAL

Melting point data were determined in open capillaries with an Electrothermal melting point apparatus and are uncorrected. The progress of reactions was followed by TLC, using silica gel with a fluorescent indicator coated on aluminium sheets. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$, using TMS as an internal standard. Elemental analyses were performed using a Carlo Erba EA 1180 element analyzer.

General procedure for the reaction of benzaldehydes with Oxone® and sodium bromide: To a stirred solutions of benzaldehydes (5 mmol) in aqueous methanol (70 mL, 1 : 1 by volume) was added NaBr (2.57 g, 25 mmol) and Oxone® (3.07 g, 5 mmol or 6.14 g, 10 mmol). The reaction was continuously monitored by thin-layer chromatography and stirred at r.t. for generally 4–24 h. The reaction mixture was quenched with aqueous sodium thiosulfate and extracted with ether (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-EtOAc 10 : 1, giving the products (Table 1).

The spectral and analytical data of products are as follows:

1a: oil (Lit.[20] b.p. 198–199°). ^{1}H NMR δ 3.91 (s, 3H), 7.40–7.55 (m, 3H), 8.02–8.06 (m, 2H).

1b: oil (Lit.[20] b.p. 212°). ^{1}H NMR δ 1.39 (t, $J = 7.2$ Hz, 3H), 4.38 (q, $J = 7.2$ Hz, 2H), 7.40–7.57 (m, 3H), 8.03–8.06 (m, 2H).

2: oil (Lit.[20] b.p. 103–104°/15 Torr). ^{1}H NMR δ 2.39 (s, 3H), 3.89 (s, 3H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.92 (d, $J = 8.0$ Hz, 2H).

3a: m.p. 51–52° (Lit.[20] b.p. 51–54°). ^{1}H NMR δ 3.99 (s, 3H), 7.01 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 1H), 8.07 (s, 1H), 9.84 (s, 1H).

3b: m.p. 98° (Lit.[21] 99–100°). ^{1}H NMR δ 3.94 (s, 3H), 4.00 (s, 3H), 6.96 (d, $J = 8.7$ Hz, 1H), 8.02 (dd, $J = 8.7$, 2.1 Hz, 1H), 8.27 (d, $J = 2.1$ Hz, 1H).

3c: m.p. 61–62° (Lit.[22] 60–61°). ^{1}H NMR δ 3.87 (s, 3H), 6.77 (d, $J = 8.8$ Hz, 1H), 7.37 (dd, $J = 8.8$, 2.3 Hz, 1H), 7.66 (d, $J = 2.3$ Hz, 1H).

4a: m.p. 115–116° (Lit.[20] 116–119°). ^{1}H NMR δ 3.93 (s, 3H), 6.90 (d, $J = 8.9$ Hz, 1H), 7.63 (dd, $J = 8.9$, 2.6 Hz, 1H), 7.91 (d, $J = 2.6$ Hz, 1H), 10.38 (s, 1H).

4b: oil (Lit.[23] m.p. 39–40°). ^{1}H NMR δ 3.89 (s, 6H), 6.87 (d, $J = 8.9$ Hz, 1H), 7.56 (dd, $J = 8.9$, 2.6 Hz, 1H), 7.91(d, $J = 2.6$ Hz, 1H).

5a: m.p. 105–108° (Lit.[24] 110°). ^{1}H NMR δ 3.94 (s, 3H), 7.40 (s, 1H), 7.84 (s, 1H), 10.26 (s, 1H).

5b: m.p. 129–130°. ^{1}H NMR δ 3.94 (s, 3H), 6.93 (d, $J = 8.7$ Hz, 1H), 7.58 (d, $J = 8.7$ Hz, 1H), 10.23 (s, 1H). Anal. calcd. for $C_8H_6Br_2O_2$: C, 32.69; H, 2.06. Found: C, 32.41; H, 1.98.

5c: m.p. 118–119° (Lit.[25] 119°). ^{1}H NMR δ 6.38 (s, 1H), 7.85 (s, 1H), 10.17 (s, 1H).

6a: m.p. 112°. ^{1}H NMR δ 2.30 (s, 3H), 7.82 (d, $J = 8.6$, 1.8 Hz, 1H), 7.88 (s, 1H), 8.08 (d, $J = 1.8$ Hz, 1H), 8.63 (d, $J = 8.6$ Hz, 1H), 9.88 (s, 1H). Anal. calcd. for $C_9H_8BrNO_2$: C, 44.66; H, 3.33; N, 5.79. Found: C, 44.39; H, 3.03; N, 5.52.

6b: m.p. 168° (Lit.[26] 165–168°). ^{1}H NMR δ 2.04 (s, 3H), 7.47 (d, $J = 8.9$ Hz, 2H), 7.56 (d, $J = 8.9$ Hz, 2H), 10.07 (s, 1H).

6c: m.p. 142–143° (Lit.[27] 144.7°). ^{1}H NMR δ 2.24 (s, 3H), 7.42 (dd, $J = 8.9$, 2.1 Hz, 1H), 7.57 (s, 1H), 7.68 (d, $J = 2.1$ Hz, 1H), 8.26 (d, $J = 8.9$ Hz, 1H).

7a: m.p. 90–93° (Lit.[28] 94°). ^{1}H NMR δ 3.90 (s, 3H), 3.96 (s, 3H), 6.95 (d, $J = 8.6$ Hz, 1H), 7.94 (dd, $J = 8.6$, 2.1 Hz, 1H), 8.05 (d, $J = 2.1$ Hz, 1H).

7b: m.p. 68–70° (Lit.[29] 70°). ^{1}H NMR δ 3.88 (s, 3H), 6.79 (d, $J = 8.7$ Hz, 1H), 7.32 (dd, $J = 8.7$, 2.3 Hz, 1H), 7.49 (d, $J = 2.3$ Hz, 1H).

8: m.p. 93–94°. ^{1}H NMR δ 3.90 (s, 3H), 3.96 (s, 3H), 6.95 (d, $J = 8.6$ Hz, 1H), 7.94 (dd, $J = 8.6$, 2.1 Hz, 1H), 8.05 (d, $J = 2.1$ Hz, 1H). Anal. calcd. for $C_{10}H_{10}ClNO_3$: C, 52.76; H, 4.43; N, 6.15. Found: C, 52.53; H, 4.18; N, 5.88.

General procedure for the reaction of benzoic acids with Oxone® and sodium bromide: To a stirred suspension of benzoic acids (5 mmol) in aqueous methanol (70 mL, 1 : 1 by volume) was added Na_2CO_3 (0.53 g, 5 mmol), NaBr (2.57 g, 25 mmol) and Oxone® (3.07 g, 5 mmol or 6.14 g, 10 mmol). The reactions were continuously monitored by thin-layer chromatography and stirred at r.t. for 24 h. The reaction mixture was quenched with aqueous sodium thiosulfate and extracted with ether (3×50 mL). The organic layers were washed with aqueous Na_2CO_3, water, dried and evaporated. The residue was chromatographed on a silica gel column and eluted with hexane-EtOAc 10 : 1 to give the aryl bromide. The combined aqueous layer was acidified with a 10% HCl solution to pH 2 and extracted with EtOAc (2×50 mL). The organic layers were washed with water, dried and evaporated to afford the acid products.

The spectral and analytical data of products are as follows:

9a: m.p. 202–204° (Lit.[30] 201–206°). ^{1}H NMR δ 3.96 (s, 3H), 6.95 (d, $J = 8.5$ Hz, 1H), 8.00 (dd, $J = 8.5$, 1.8 Hz, 1H), 8.22 (d, $J = 1.8$ Hz, 1H), 9.22 (brs, 1H).

9b: oil (Lit.[22] b.p. 124°/40 Torr). ^{1}H NMR δ 3.76 (s, 3H), 6.77 (d, $J = 8.9$ Hz, 2H), 7.36 (d, $J = 8.9$ Hz, 2H).

10a: m.p. 220–221° (Lit.[31] 226–229°). ^{1}H NMR δ 2.27 (s, 3H), 7.97 (dd, $J = 8.5$, 1.8 Hz, 1H), 8.12 (s, 1H), 8.23 (d, $J = 1.8$ Hz, 1H), 8.35 (d, $J = 8.5$ Hz, 1H).

11: m.p. 148–150° (Lit.[27] 151.4°). ^{1}H NMR δ 2.24 (s, 3H), 7.39 (dd, $J = 8.9$, 2.1 Hz, 1H), 7.52 (d, $J = 2.1$ Hz, 1H), 7.57 (s, 1H), 8.29 (d, $J = 8.9$ Hz, 1H).

12: m.p. 119–120° (Lit.[23] 119°). ^{1}H NMR δ 4.07 (s, 3H), 6.97 (d, $J = 8.9$ Hz, 1H), 7.67 (dd, $J = 8.9$, 2.4 Hz, 1H), 8.27 (d, $J = 2.4$ Hz, 1H), 10.23 (brs, 1H).

13: m.p. 201–202° (Lit.[32] 198°). ^{1}H NMR δ 3.92 (s, 3H), 7.44 (s, 1H), 7.82 (s, 1H).

14a: m.p. 204–205° (Lit.[33] 204–205°). ^{1}H NMR δ 2.45 (s, 3H), 7.30 (d, $J = 7.9$ Hz, 1H), 7.88 (dd, $J = 7.9$, 1.5 Hz, 1H), 8.20 (d, $J = 1.2$ Hz, 1H).

14b: m.p. 60–61° (Lit.[34] 61°). ^{1}H NMR δ 4.43 (s, 2H), 7.26 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 2H).

REFERENCES

1. (a) Kennedy, R.J.; Stock, A.M. J. Org. Chem. **1960**, *25*, 1901; (b) Adam, W.; Hadjiarapoglou, L.; Smerz, A. Chem. Ber. **1991**, *124*, 227.
2. Jeyaraman, R.; Murray, R.W. J. Am. Chem. Soc. **1984**, *106*, 2462.
3. Zabrowski, D.L.; Moormann, A.E.; Beck, K.R.J. Tetrahedron Lett. **1988**, *29*, 4501.
4. Davis, F.A.; Chattopadhyay, S.; Towson, J.C.; Lal, S.; Reddy, T. J. Org. Chem. **1988**, *53*, 2087.
5. Greenhalgh, R.P. Synlett. **1992**, 235.
6. Ceccherelli, P.; Curini, M.; Epifano, F.; Marcotullio, M.C.; Rosati, O. J. Org. Chem. **1995**, *60*, 8412.
7. Paradkar, V.M.; Latham, T.B.; Demko, D.M. Synlett. **1995**, 1059.
8. Curini, M.; Epifano, F.; Marcotullio, M.C.; Rosati, O. Synlett. **1999**, 777.
9. Ceccherelli, P.; Curini, M.; Marcotullio, M.C.; Epifano, F.; Rosati, O. Synlett. **1996**, 767.
10. Subhas Bose, D.; Srinivas, P. Synth. Commun. **1997**, *27*, 3835.
11. Ceccherelli, P.; Curini, M.; Epifano, F.; Marcotullio, M.C.; Rosati, O. Synth. Commun. **1998**, *28*, 3057.
12. Dieter, R.K.; Nice, L.E.; Velu, S.E. Tetrahedron Lett. **1996**, *37*, 2377.

13. Ross, S.A.; Burrows, C.J. Tetrahedron Lett. **1997**, *38*, 2805.
14. Williams, D.R.; Klingler, F.D.; Allen, E.E.; Lichtenthaler, F.W. Tetrahedron Lett. **1988**, *29*, 5087.
15. Direct Oxidation of *p*-anisaldehyde with Bromine in Methanol Afforded Methyl *p*-anisate in 50% yield, See Ref. [14].
16. Webb, K.S.; Ruszkay, S.J. Tetrahedron Lett. **1998**, *54*, 401.
17. Castellani, C.B.; Carugo, O.; Giusti, M.; Leopizzi, C.; Perotti, A.; Invernizzi, A.G.; Vidari, G. Facile Decarbonylation of Some Electron-Rich Aromatic Aldehydes in the Presence of $Sc(OTf)_3$. Tetrahedron **1996**, 52, 11045.
18. (a) Johnson, R.G.; Ingham, R.K. Chem. Rev. **1956**, *56*, 219; (b) Wilson, C.V. Org. React. (N.Y.) **1957**, *9*, 332; (c) Sheldon, R.A.; Kochi, J.K. Org. React. (N.Y.) **1972**, *19*, 279; (d) Barton, D.H.R.; Faro, H.P.; Serebryakov, E.P.; Woolsey, N.F. J. Chem. Soc. **1965**, 2438; (e) Cristol, J.S.; Firth, W.C. J. Org.Chem. **1961**, *26*, 280; (f) Oldham, J.W.H.; Ubbelohde, A.R. J. Chem. Soc. **1941**, 368; (g) McKillop, A.; Bromley, D.; Taylor, E.C. J. Org. Chem. **1969**, *34*, 1172; (h) Kochi, J.K. J. Am. Chem. Soc. **1965**, *87*, 2500; (i) Patrick, T.B.; Johri, K.K.; White, D.H. J. Org. Chem. **1983**, *48*, 4158; (j) Roy, S.; Chowdhury, S. J. Org. Chem. **1997**, *62*, 199; (k) Naskar, D.; Chowdhury, S.; Roy, S. Tetrahedron Lett. **1998**, *39*, 699; (l) Naskar, D.; Roy, S. Tetrahedron **2000**, *56*, 1369.
19. Chlorodecarbonylation and Chlorodecarboxylation Using Oxone® and NaCl Occurred in Unacceptable Yield, but Iododecarbonylation and Iododecarboxylation Using Oxone® and NaI did not Occur.
20. Aldrich Catalogue 2000. Published by Aldrich Chemical Co., Inc.
21. Jagannadha Rao, K.V.; Ramachandra Row, L. J. Org. Chem. **1960**, *25*, 981.
22. Kajigaeshi, S.; Moriwaki, M.; Tanaka, T.; Fujisaki, S.; Kakinami, T.; Okamoto, T. J. Chem. Soc. Perkin Trans. 1 **1990**, 897.
23. Baddar, F.G.; Fahim, H.A.; Fleifel, A.M. J. Chem. Soc. **1955**, 2199.
24. Hodgson, H.H.; Beard, H.G. J. Chem. Soc. **1925**, 875.
25. Brink, M. Acta Univ. Lund. Sect. 2 **1965**, 1; C. A. **1965**, *63*, 8240c.
26. Hazlet, S.E.; Dornfeld, C.A. J. Am. Chem. Soc. **1944**, *66*, 1781.
27. Owen, G. J. Chem. Soc. **1923**, 3392.
28. Sorensen, P. Anal. Chem. **1955**, *27*, 391.
29. Kohn, M.; Sussmann, J.J. Monatsh **1927**, *48*, 193; C. A. **1927**, *21*, 3605.
30. Wyrick, S.D.; Smith, F.T.; Kemp, W.E.; Grippo, A.A. J. Med. Chem. **1987**, *30*, 1798.
31. Chas. Raiford, L.; Davis, H.L. J. Am. Chem. Soc. **1927**, *50*, 156.
32. Patel, S.R.; Nargund, K.S. J. Indian Chem. Soc. **1955**, *32*, 187; C. A. **1956**, *50*, 4959b.

33. Crandall, E.W.; Beasley, R.; Lambing, L.L.; Moriconi, R. J. Org. Chem. **1967**, *32*, 134.
34. Weizmann, M.; Patai, S. J. Am. Chem. Soc. **1946**, *68*, 150.

Received in the UK November 11, 2000