Tetrahedron 75 (2019) 130573

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A transition metal free expedient approach for the C=C bond cleavage of arylidene Meldrum's acid and malononitrile derivatives

Muthiah Suresh, Anusueya Kumari, Raj Bahadur Singh*

Department of Chemistry, Central University of Jharkhand, Brambe, Ranchi, 835 205, India

ARTICLE INFO

Article history:
Received 4 July 2019
Received in revised form
16 August 2019
Accepted 29 August 2019
Available online 4 September 2019

Keywords:
Arylidine Meldrum's acid
Arylidinemalononitrile
Oxidative C=C bond cleavage
PIDA
Oxone

ABSTRACT

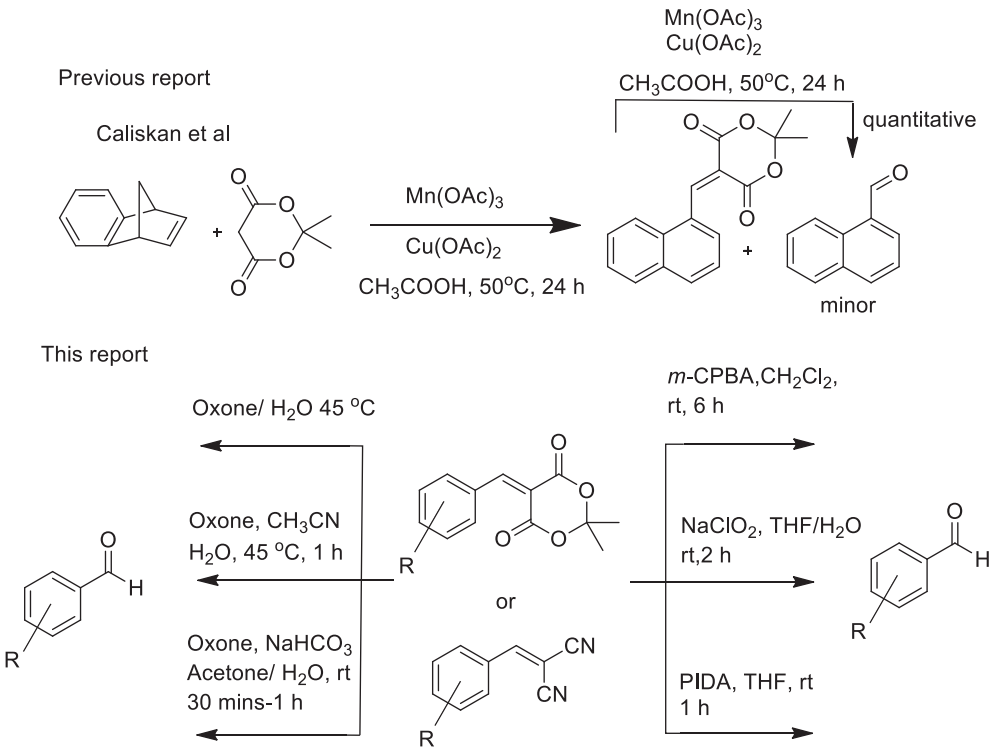
A transition metal free expedient approach for the C=C bond cleavage of electron deficient alkenes such as arylidene Meldrum's acid and malononitrile derivatives are discussed. The C=C bond of these compound were cleaved to benzoic acid in good yield at high temperature. Most importantly, with oxone in CH_3CN/H_2O at 45 °C or *m*-CPBA in DCM or $NaClO_2$ in THF/H_2O or PIDA in THF at room temperature furnished benzaldehyde derivatives selectively in excellent yields.

1. Introduction

Structurally diverse alkenes from natural products have been considered to be a suitable source for the synthesis of complex molecules [1]. Transforming the alkenes to carbonyls or carboxyl compounds via oxidative cleavage have greatly received the attention of chemists for their extensive application in organic chemistry [2]. Normally, the oxidative cleavage of the C=C bond is instigated by transition metal and non-metal oxidants and helps to incorporate the oxo group [3]. However, the formation of toxic by-products restricts the usage of metal oxidants. Response to such a problem is abetted to develop various sustainable approaches for cleaving the electron-rich C=C bond [4]. In 2010, Vinod et al. reported the facile approach to cleave a C=C bond of electron rich as well as electron deficient olefins by using the water-soluble in-situ generated hypervalent iodine reagent. Moorthy et al. reported the oxone mediated oxidative cleavage of various electron deficient olefins to afford the corresponding benzoic acids [5]. Like electron rich olefins, electron deficient olefins such as arylidene Meldrum's acid, malononitrile, diethyl malonate derivatives have been used in the synthesis of various synthetically important molecular scaffolds [6]. In 2001, Tsuno et al. reported that epoxidation of arylidenene Meldrum's acid can be obtained with H_2O_2 [7]. Similarly, McQuaid et al. showed that epoxidation of various conjugated diester can be achieved with iodosylbenzene [8]. Notably, no oxidative cleavage product of these molecules were observed. However, Caliskan et al. reported (Scheme 1) the $Mn(OAc)_3$ and $Cu(OAc)_2$ mediated unusual transformation of Meldrum's acid derivative as well as diethylmalonate derivative of naphthaldehyde to 1-naphthaldehyde [9]. In our previous report, we used the oxone for the epoxidation of styrene derivative and obtained it in good yield [10]. In turn, we attempted to the epoxidation of arylidene Meldrum's acid derivative with oxone at room temperature. Surprisingly, we found that the starting material was consumed in short time and provided selectively aldehyde as a major product. These results intrigued us to investigate oxidative cleavage reaction of electron deficient olefins of arylidene Meldrum's acid, malononitrile derivatives by using various water-soluble and insoluble oxidants [11]. Unlike styrene or cinnamates, arylidene Meldrum's acid, malononitrile and diethylmalonate derivatives exhibit highly reactive benzylic carbon which is inclined to act as a strong Michael acceptor [6]. Hence, cleaving such C=C bond needed mild conditions to selectively afford the corresponding aldehyde. Herein, mild and efficient methods for the oxidative cleavage of the electron deficient C=C bond of arylidene Meldrum's acid, malononitrile derivatives with oxidants Oxone or *m*-CPBA or $NaClO_2$ or PIDA are demonstrated.

* Corresponding author. ,
E-mail addresses: rajbahadur.iitb@gmail.com, raj.singh@cuj.ac.in (R.B. Singh).

https://doi.org/10.1016/j.tet.2019.130573
0040-4020/



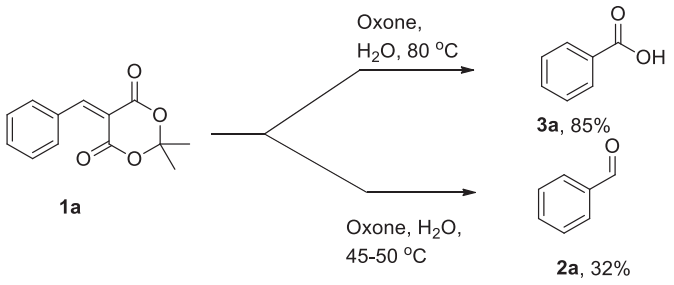
Scheme 1. Oxidative cleavage of C=C bond of arylidene Meldrum's acid.

2. Results and discussion

At first, the oxidative cleavage of C=C bond of compound **1a** was executed with oxone in water at 80 °C (Scheme 2). Unexpectedly, the reaction provided the benzoic acid **3a** as a major product in 2 h. Encouraged by this result, we made several attempts to selectively produce the aldehyde and found that oxidative cleavage of C=C of **1a** with 3 eq. of oxone in water at 45 °C for 2 h provided the aldehyde **2a** in 32% yield. However, heating for prolonged period afforded the corresponding acid **3a**. Similarly, other water soluble peroxides $(NH_4)_2S_2O_8$, $K_2S_2O_8$, and H_2O_2 provided **2a**, and **3a**. The results were encouraging; however the careful observation of this process indicated that harsh reaction condition and poor solubility of arylidene Meldrum's acid derivatives in water as a sole solvent were seems to afford the low yield of aldehydes.

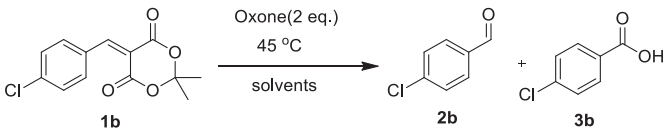
Then we employed oxone in mixed solvents to improve the solubility of arylidene Meldrum's acid derivatives to increase the efficiency of the reaction. Hence, we investigated the reaction of **1b** with oxone in CH_3CN/H_2O mixture at room temperature [5b,11b]. Disappointingly, the reaction was sluggish and afforded the aldehyde in 20% yield after 16 h. However, heating at 45 °C employed a distinguishable impact on the oxidative cleavage and it furnished the desired product **2b** in 88% yield (Table 1). Prolonged exposure of **1b** with oxone at 45 °C led to the formation of overoxidised product **3b** in 28% yield. On the other hand, refluxing the reaction mixture for 8 h furnished **3b** as the sole product in excellent yield.

Then we explored the C=C bond cleavage in various solvent mixture and the results are depicted in Table 1. In case of water miscible mixture, the oxidative cleavage proceeded smoothly and afforded the aldehyde in good yield (Table 1, entry 2, 4). However, competing side product **3b** was observed, while the reaction was performed in 1,4-dioxane/H_2O mixture. In contrast, with solvent DCE/H_2O or CH_2Cl_2/H_2O mixture the negligible conversion was observed. Undoubtedly, an immiscible biphasic solvent mixture reduced the contact between the substrate and oxidants. The above



Scheme 2. Cleavage of C=C bond to afford aldehyde.

Table 1
The oxidative cleavage reaction of C=C bond with oxone at **45 °C**.



Sl.No	Solvents (1:1)	Conditions	Time (h)	Yield (%) 2b	Yield (%) 3b
1	CH_3CN/H_2O	45 °C	1	88	–
2	CH_3OH/H_2O	45 °C	1	75	–
3	1,4-dioxan/H_2O	45 °C	3	55	22
4	THF/H_2O	45 °C	1	73	–
5	CH_3NO_2/H_2O	45 °C	3	55	–
6	2-propanol/H_2O	45 °C	3	36	–
7	CH_3CN/H_2O	45 °C	16	65	28
8	CH_3CN/H_2O	reflux	8	–	86
9	DCE/H_2O	45 °C	6	–	–
10	CH_2Cl_2/H_2O	45 °C	2	–	–

stated results clearly indicates that the temperature as well as nature of the solvent has influenced the selectivity of the product on the oxidative cleavage of the C=C bond. In continuation, the cleavage of C=C bond of **1b** was examined with other oxidents such as persulfates, $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ in CH_3CN/H_2O (1:1) at 45 °C (Table 2). Notably, these oxidants also effectively generated the aldehyde in good yield. However, along with aldehyde significant amount of over oxidized product **3b** was also obtained in some cases (Table 2, entries 2,3). In case of H_2O_2, the reaction furnished the aldehyde **2b** in moderate yield along with the unreacted starting material. Furthermore, we found that the combination of oxone with $NaHCO_3$ in acetone/H_2O (Table 2, entry 7) was also suitable for the cleavage of the electron deficient C=C bond [12].

Generally, $NaClO_2$ is known for epoxidation of styrene, allylic oxidation, and oxidation of aldehyde to carboxylic acid [13]. However, $NaClO_2$ cleaved the C=C bond of **1b** and selectively afforded the aldehyde **2b** in 78% yield. After a detailed study with various solvent mixture and oxidants, the scope of this C=C bond cleavage was explored with a series of arylidene Meldrum's acid derivatives and other electron deficient alkenes (Table 3). As mentioned in Table 3, under optimized reaction condition the C=C bond of arylidene Meldrum's acid derivatives were effectively cleaved to afford the aldehyde in excellent yield. We also examined (Table 3) the oxidative cleavage reaction with other electron deficient molecules such as chalcones, cinnamic acid and arylidene derivative of diethyl malonate, malononitrile. Like arylidene Meldrum's acid derivatives, C=C bond of diethyl malonate derivative and malononitrile derivatives were effectively cleaved to afford the aldehyde in good yield. In case of chalcone and cinnamic acid, we have not observed the corresponding C=C bond cleaved product at low temperature with stoichiometric amount of oxidants. As stated in reports by vinod et al. [5a] and Moorthy et al. [5b], the conjugated carbonyl groups needed longer reaction duration and high temperature for the cleavage of C=C bond. Hence, with excess of oxidants at refluxing condition, the C=C bond of cinnamic acid as well as chalcone was cleaved to provide the benzoic acid in good yield [5b].

We next explored C=C bond cleavage with organic peroxide *m*-CPBA [11e,14]. Generally, *m*-CPBA has been used for the epoxidation of electron rich olefins and reacts moderately with electron deficient olefins such as chalcones and cinnamates [15]. To our delight, the reaction of **1b** in DCM was provided the aldehyde **2b** in excellent yield (Table 4). Moreover, the cleavage of a C=C bond of malononitrile derivatives was pleasingly furnished the aldehyde in good yield.

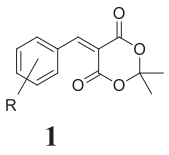
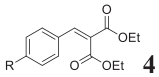
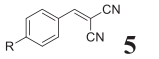
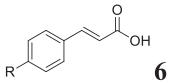
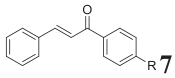
Having established various approaches by using peroxides and sodium chlorite for the cleavage of electron deficient C=C bond, we further inspected a metal-free and efficient approach using phenyliodine(III)diacetate (PIDA) [16].

Table 2
Reaction of **1b** with other oxidants.

Entry	Oxidants	Conditions	Time (h)	Yield (%) 2b	Yield (%) 3b
1	Oxone	45 °C	1	88[a]	–
2	$K_2S_2O_8$	45 °C	3	65[a]	27
3	$NH_4S_2O_8$	45 °C	3	62[a]	30
4	H_2O_2	45 °C	4	55[a]	–
5	$NaClO_2$	45 °C	1	78[a]	–
6	$NaClO_2$	rt	2	73[b]	–
7	Oxone	rt	1	85[c]	–

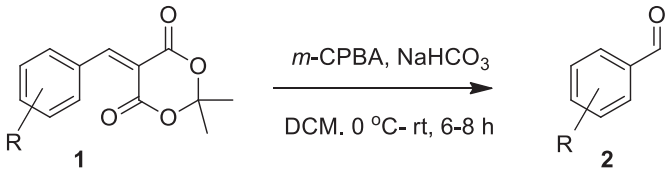
Conditions:
[a] The reaction performed in CH_3CN/H_2O at 45 °C.
[b] the reaction was performed in THF.
[c] The reaction was performed with oxone (2.5eq.)/$NaHCO_3$ (4 eq.) in acetone/H_2O (2:1).

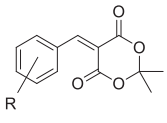
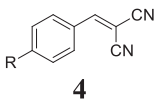
Table 3
Scope of the cleavage of C=C bond.

Substrate	Functional group	Yield of aldehyde	Yield of acid
R=  1	H	2a, 86%	3a, 89%[b]
	4-Cl	2b, 88%	3b, 86%[b]
	2-Cl	2c, 86%	
	4-Br	2d, 90%	
	2-Br	2e, 87%	3e, 91%[b]
	4-Me	2f, 91%	
	4-OMe	2g, 89%	
	3,4-*di*-OMe	2 h, 90%	
	3,4,5-*tri*-OMe	2i, 91%	
	2,5-*di*-OMe	2j, 84%	
	2-OMe	2k,84%	
	2-Br-5-OMe	2l, 85%	
	4-NO_2	2m,75%	3m, 69%[c]
	3,5-*di*-OMe	2n, 91%	3n, 65%[b]
	4-N,N-*di*-Me	2°, 89%	
	3-OMe	2p, 90%	
	3-OMe-4-OH	2q, 72%	
 4	H	2a, 84%	
 5	H	2a, 70%,	3a, 90%[b]
	4-Cl	2b, 68%	3b, 88%[b]
 6	H	Not observed	3a, 90%[b]
 7	H	Not observed	3a, 67%[b]

[a]Conditions: oxone (2 eq.), CH_3CN/H_2O, 45 °C for 1 h.
[b] Used 6eq. of oxone and refluxed for >16 h.
[c] Stirred at 45 °C for 12 h.

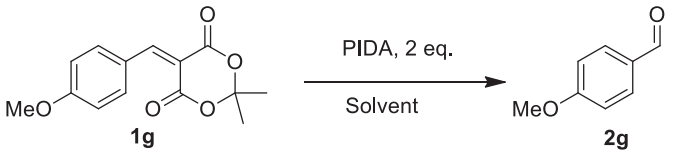
Table 4
Reaction with organic peroxides.



Substrate	Substitution	Yield of Aldehyde
 1	4-Cl	2b, 90%
	4-OMe	2g, 86%
	3,4-di-OMe	2 h, 87%
	2,5-di-OMe	2j, 83%
	3,4,5-tri-OMe	2i, 85%
 4	H	2a, 78%
	4-Cl	2b, 76%

Fortunately, the C=C bond cleavage of **1g** with PIDA in DCM proceeded smoothly at room temperature and afforded the aldehyde **2g** in 56% yield. Surprised by the results, we next studied the cleavage of C=C bond of **1g** with PIDA in different solvents. PIDA (2 eq.) in THF was effectively cleaved the C=C bond of **1g** and exclusively provided the aldehyde in 89% yield (Table 5). Notably, with other hypervalent iodine reagens such as, DMP and in-situ

Table 5
Reaction with hypervalent iodine reagents.



Entry	oxidants	Co-oxidants	Solvent	Time (mins)	Yield (%)
1	PIDA	–	DCM	120	56
2	PIDA	–	THF	45	89
3	PIDA	–	CH_3CN	120	80
4	DMP	–	THF	360	nr
5	*p*-IBA	NMO	DCM	360	nr

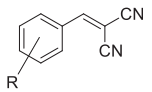
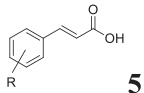
generated iodoxobenzoic acid [5a,17] (i.e mixture of *p*-IBA and 2 eq. of NMO) **2g** were ineffective. Further, we decided to explore the oxidative cleavage of malononitrile derivatives with PIDA in THF. To our delight, the PIDA involved C═C bond scission of malononitrile derivative provided comparatively better yield than other oxidants and the results are summarized in Table 6.

3. Plausible mechanism

From various experiments, we observed that the C═C bond of arylidene Meldrum's acid derivatives can be effectively cleaved with peroxides, $NaClO_2$, and PIDA to afford selectively the corresponding benzaldehydes. The C═C bond cleavage with these oxidants quickly furnished the aldehydes. Controlled experiments by lowering the oxidants and the reaction time minimize the immediate C═C bond cleavage to aldehyde. Unluckily, while purification we found that the intermediate was decomposed and afforded the aldehyde. However, the available literature sources have supported to develop the plausible mechanism [5b,7,8,18]. Commonly, the oxidation of double bond of all substrates with peroxides proceed via epoxidation and further the oxirane ring cleavege to form the diol under the developed reaction conditions. However, we assume that the C═C bond cleavage of arylidene Meldrum's acid with oxone in CH_3CN–H_2O proceeds via diol formation and followed by the C–C single bond cleavage as shown by the Moorthy et al (Scheme 3). [5b].

In case of PIDA mediated reaction [19], first it activates benzylic position of arylidene Meldrum's acid by interacting with carbonyl oxygen and followed by the Michael addition generates the β-acetylated species (Scheme 4). Further attack by carbonyl oxygen of acetyl group leads to intramolecular cyclization and form the acetyloxonium ion of Meldrum's acid derivative. Presence of water in the reaction medium support to provide the α-actylated-β-hydroxy alkylidene Meldrum's acid. Further cleavage of C–C bond provides the carbonyl compound.

Table 6
Reaction of PIDA with arylidenemalononitrile derivative.

Substrate	Substitution	Time (mins)	Yield of aldehyde
	4-Cl	45	2b, 89%
	4-Me	45	2f, 91%
	3,4-*di*-OMe	60	2 h, 82%
	2,5-*di*-OMe	60	2j, 78%
4	2-OMe	60	2k, 77%
	H	300	No reaction
5			

In conclusion, we have developed multiple approaches involving various oxidants for the oxidative cleavage of C═C of arylidene Meldrum's acid and malononitrile derivatives to the corresponding aldehyde. The advantages of these methods are as follows: (1) the cleavage of C═C bond proceeds under mild condition with various oxidants in short reaction time; (2) the C═C bond can be cleaved without addition of any transition metal catalyst; (3) PIDA cleaves the C═C bond of malononitrile derivatives effectively.

4. Experimental section

Reagents and solvents were purchased from commercial sources and used without further purification. All the reactions were monitored by TLC, performed on 0.25 mm silica gel coated aluminium sheets (F-254) and visualized by UV light and $KMnO_4$ solution. Column chromatography was carried out using silica gel (100–200 mesh). ^1H NMR spectra were recorded in solvent $CDCl_3$ on 300, 400 MHz Bruker-AVANCE and 400 MHz JEOL spectrometers with TMS as an internal standard.

4.1. Synthesis of substrate

Starting materials arylidene Meldrum's acid, malononitrile derivatives were synthesized by a modified procedure reported by Bigi et al. [20,21] Thus the mixture of aldehyde and Meldrum's acid or malononitrile in H_2O was stirred at room temperature for 12 h to afford the corresponding product. Diethylmalonate derivatives, cinnamic acid and chalcones were prepared according to reported procedure [22–24].

4.2. General procedure for oxidative cleavage by oxone to afford acid 3

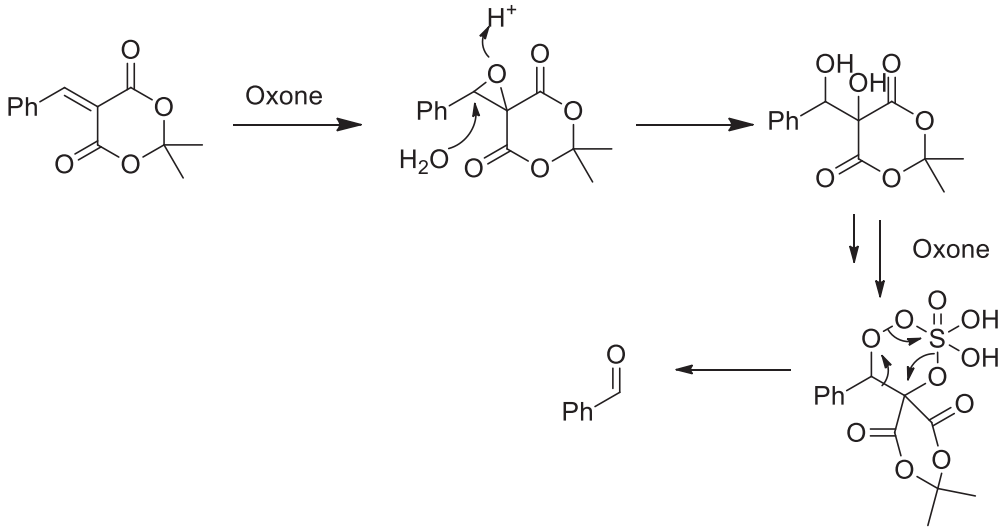
To a heterogeneous mixture of arylidene meldrum's acid or malononitrile derivatives in distilled water, Oxone (3 eq) was added and heated at 80 °C for 2 h. The progress of the reaction was monitored by the TLC and after completion saturated NH_4Cl solution was added and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and purified by column chromatography to isolate the pure product.

4.3. General procedure for oxidative cleavage by oxone to afford aldehyde 2

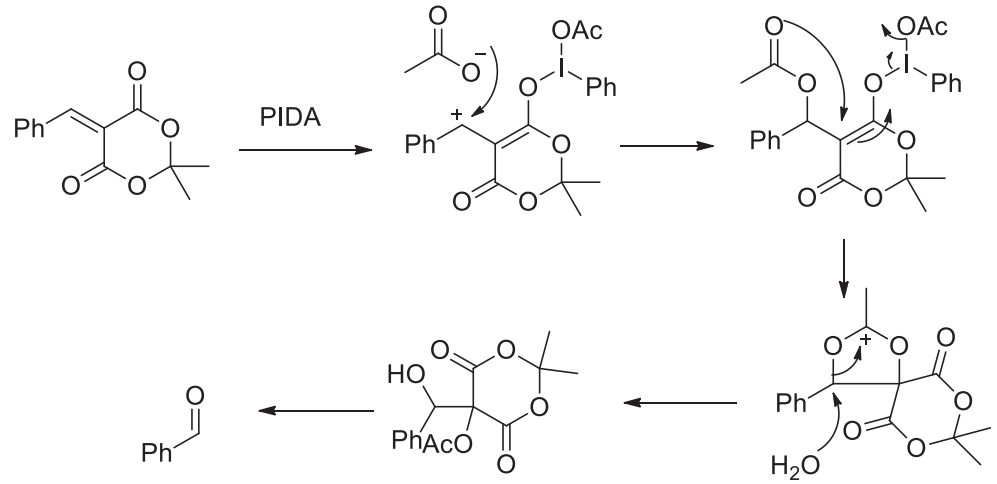
To a heterogeneous mixture of arylidene meldrum's acid or malononitrile derivatives in distilled water, Oxone (2.5 eq) was added and heated at 45 °C for 2 h. The progress of the reaction was monitored by the TLC. After 2 h, saturated $NaHCO_3$ solution was added to the reaction mixture and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and purified by column chromatography to isolate the pure aldehyde.

4.4. General procedure for oxidative cleavage by oxone in CH_3CN/H_2O to afford aldehyde 2

Oxone (2.5 eq) was added to the solution of Arylidene meldrum's acid or malononitrile derivatives in CH_3CN/H_2O (1:1) and heated the reaction mixture at 45 °C for 1 h. The progress of the reaction was monitored by the TLC. After completion, ethyl acetate was added to the reaction mixture and separated the organic layer. The organic layer was washed thrice with saturated $NaHCO_3$ solution and followed by distilled water. The organic layer was dried over anhydrous Na_2SO_4 and filtered through silica gel plug. The



Scheme 3. Plausible mechanism of oxidative cleavage of arylidene Meldrum's acid with oxone.



Scheme 4. Plausible mechanism of oxidative cleavage of arylidene Meldrum's acid with PIDA.

resulted organic layer was evaporated to afford the pure aldehyde in good yield.

4.5. General procedure for oxidative cleavage by oxone in acetone/H_2O to afford aldehyde 2

Oxone (2.5 eq) and $NaHCO_3$ (4 eq) was added to the solution of Arylidene Meldrum's acid or malononitrile derivatives in acetone/H_2O (2:1) and a brisk effervescence was observed. The reaction mixture was stirred at room temperature for 30 mins-1h. The progress of the reaction was monitored by the TLC. After completion, ethyl acetate was added to the reaction mixture and separated the organic layer. The organic layer was washed with saturated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4 and evaporated under vacuum to afford the aldehyde.

4.6. General procedure for oxidative cleavage by $NaClO_2$ in THF/H_2O to afford aldehyde 2

$NaClO_2$ (2 eq) was added to the solution of arylidene meldrum's acid or malononitrile derivatives in THF/H_2O (1:0.5) and stirred the reaction mixture at room temperature for 1–2 h. The progress of the reaction was monitored by the TLC. After completion, the organic layer was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by column chromatography to afford the corresponding aldehyde.

4.7. General procedure for oxidative cleavage by m-CPBA in CH_2Cl_2 to afford aldehyde 2

Arylidene meldrum's acid or malononitrile derivative was dissolved in CH_2Cl_2. To this *m*-CPBA (2 eq) and $NaHCO_3$ (3 eq) were added and stirred the reaction mixture for 5–6 h. The progress of the reaction was monitored by the TLC. After completion, distilled water was added to the reaction mixture and the organic layer was extracted with CH_2Cl_2. The dried organic layer was evaporated under vacuum and purified by column chromatography to afford the corresponding aldehyde.

4.8. General procedure for oxidative cleavage by PIDA in THF to afford aldehyde 2

PIDA (2 eq) was added to the solution of arylidene meldrum's

acid or malononitrile derivatives in THF and stirred the reaction mixture at room temperature for 45 mins- 1 h. The progress of the reaction was monitored by the TLC. After completion, saturated $NaHCO_3$ solution was added to the reaction mixture and extracted with ethyl acetate. The vacuum dried organic residue was subjected to column chromatography to afford the corresponding aldehyde.

4.9. Characterization data of corresponding oxidation products

Benzaldehyde **2a.** Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.02 (s, 1H), 7.89 (t, J = 8 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 8 Hz, 2H).

4-Chlorobenzaldehyde **2b**. Colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.99 (s, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H).

2-Chlorobenzaldehyde **2c**. Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.50 (s, 1H), 7.93(dd, J = 7.7, 1.7 Hz, 1H), 7.54-7.52 (m, 1H), 7.46(dd, J = 8, 1 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H).

4-Bromobenzaldehyde **2d**. Colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.98 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H).

2-Bromobenzaldehyde **2e**. Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ10.37 (s, 1H), 7.93-7.91 (m, 1H), 7.66 (d, J = 8 Hz, 1H), 7.46-7.44 (m, 2H).

4-Methylbenzaldehyde **2f**. Light brown liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.96 (s, 1H), 7.78 (d, J = 4 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 2.44 (s, 3H).

4-Methoxybenzaldehye **2g**. Light brown liquid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.89 (s, 1H), 7.84 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H).

3,4-Dimethoxybenzaldehyde **2h**. Solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.77 (s, 1H), 7.39(dd, J = 8, 4 Hz, 1H), 7.33 (d, J = 1.6 Hz, 1H), 6.91 (d, J = 8 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H).

3,4,5-Trimethoxybenzaldehyde **2i**. Colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.87(s, 1H), 7.14(s, 2H), 3.94(2s, 9H)

2,5-Dimethoxybenzaldehyde **2j**. Solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.40 (s, 1H), 7.28 (d, J = 3.2 Hz, 1H), 7.09(dd, J = 8.8, 3.2 Hz, 1H), 6.90 (d, J = 8.8 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H).

2-Methoxybenzaldehyde **2k**. Colorless crystalline solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.45 (s, 1H), 7.81(dd, J = 7.6, 1.6 Hz, 1H), 7.56-7.51 (m, 1H), 7.03-6.96 (m, 2H), 3.91 (s, 3H).

2-Bromo-5-methoxybenzaldehyde **2l** [25]. Light brown solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.87 (s, 1H), 10.31 (s, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.41 (d, J = 3.2 Hz, 1H), 7.03(dd, J = 8.8, 3.2 Hz, 1H), 3.84 (s,3H).

4-Nitrobenzaldehyde **2m**. Brown solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.17 (s, 1H), 8.40 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H).

3,5-Dimethoxybenzaldehyde **2n**. White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.91 (s, 1H), 7.02 (d, J = 2.4 Hz, 2H), 6.71 (t, J = 2.4 Hz, 1H), 3.85 (s, 6H).

4-N,N-dimethylbenzaldehyde **2o**. Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.74(s, 1H), 7.73(d, J = 9 Hz, 2H), 6.70(d, J = 9 Hz, 2H).

3-Methoxybenzaldehyde **2p**

Brown liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.98 (s, 1H), 7.46-7.45 (m, 2H), 7.40 (d, J = 2.1 Hz, 1H), 7.20-7.17 (m, 1H), 3.87 (s, 3H).

4-Hydroxy-3-methoxybenzaldehyde **2q**. White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.83(s, 1H), 7.44-7.42(m, 2H), 7.04(d, J = 8.5 Hz, 1H), 3.96(s, 3H)

Benzoic acid **3a**. Colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (d, J = 7.1 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H).

4-Chlorobenzoic acid **3b**. Colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H).

2-Bromobenzoic acid **3e**. Colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01(dd, J = 5.1, 4 Hz, 1H), 7.72(dd, J = 7.1, 2 Hz, 1H), 7.41-7.38 (m, 2H).

4-Nitrobenzoic acid **3m**. White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.33 (d, J = 8.9 Hz, 2H), 8.27 (d, J = 9 Hz, 2H).

3,5-Dimethoxybenzoic acid **3n**. White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 (d, J = 2.4 Hz, 2H), 6.7 (t, J = 2.3 Hz, 1H), 3.85 (s, 6H).

Acknowledgements

The authors thank the Department of Science and Technology, New Delhi, India, for financial support for the projects SB/FT/CS-045/2013, EMR/2017/001292 and SAIF-CDRI Lucknow, India, for the instrumentation facility. M.S. thanks the UGC for the Senior Research Fellowship, and A.K. thanks the Central University of Jharkhand for the fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.130573.

References

[1] (a) A. Arora, Hydrocarbons (Alkanes, Alkenes and Alkynes), Discovery Publishing House, New Delhi, India, 2006;
(b) B.M. Trost, C.-J. Li (Eds.), Modern Alkyne Chemistry: Catalytic and Atom-Economic Transformations, Wiley-VCH, Weinheim, Germany, 2014;
(c) H. Yun, S.J. Danishefsky, J. Org. Chem. 68 (2003) 4519–4522;
(d) H. Yun, T.C. Chou, H. Dong, Y. Tian, Y.M. Li, S.J. Danishefsky, J. Org. Chem. 70 (2005) 10375–10380.

[2] (a) Y. Zhou, C. Rao, S. Mai, Q. Song, J. Org. Chem. 81 (2016) 2027–2034;
(b) Y. Ding, H. Li, Y. Meng, T. Zhang, J. Li, Q.-Y. Chen, C. Zhu, Org. Chem. Front. 4 (2017) 1611–1614;
(c) G. Urgoitia, R. SanMartin, M.T. Herrero, E. Domingueza, Adv. Synth. Catal. 358 (2016) 1150–1156;
(d) G. Urgoitia, R. SanMartin, M.T. Herrero, E. Domingueza, ACS Catal. 7 (2017) 3050–3060;
(e) Y. Imada, Y. Okada, K. Noguchi, K. Chiba, Angew. Chem. 131 (2019) 131–135;
(f) A.E. Kerenkan, F. Francois Beland, T.-O. Do, Catal. Sci. Technol. 6 (2016) 971–987.

[3] (a) J.R. Henry, S.M. Weinreb, J. Org. Chem. 58 (1993) 4145;
(b) B.R. Travis, R.S. Narayan, B. Borhan, J. Am. Chem. Soc. 124 (2002) 3824–3825;
(c) X. Baucherel, J. Uziel, S. Juge, J. Org. Chem. 66 (2001) 4504–4510;
(d) S.-T. Liu, K.V. Reddy, R.-Y. Lai, Tetrahedron 63 (2007) 1821–1825;
(e) A. Wang, H. Jiang, J. Org. Chem. 75 (2010) 2321–2326;
(f) V. Kogan, M.M. Quintal, R. Neumann, Org. Lett. 7 (2005) 5039–5042;
(g) D. Xing, B. Guan, G. Cai, Z. Fang, L. Yang, Z. Sh, Org. Lett. 8 (2006) 693–696;
(h) A. Dhakshinamoorthy, K. Pitchumani, Tetrahedron 62 (2006) 9911–9918;
(i) M.M. Hossain, S.-G. Shyu, Tetrahedron 70 (2014) 251–255;
(j) C. Mi, L. Li, X.-G. Meng, R.-Q. Yang, X.-H. Liao, Tetrahedron 72 (2016) 6705–6710;
(k) Z. Saedi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, Catal. Commun. 17 (2012) 18–22;
(l) A. Dhakshinamoorthy, M. Alvaro, H. Garcia, ACS Catal. 1 (2011) 836–840.

[4] (a) C.-M. Ho, W.-Y. Yu, C.-M. Che, Angew. Chem. Int. Ed. 116 (2004) 3365–3369;
(b) K. Miyamoto, N. Tada, M. Ochiai, J. Am. Chem. Soc. 129 (2007) 2772–2773;
(c) K. Miyamoto, Y. Sei, K. Yamaguchi, M. Ochiai, J. Am. Chem. Soc. 131 (2009) 1382–1383;
(d) J.-P. Wan, A.C. Nelson, E.S. Kalinowski, N.J. Czerniecki, T.L. Jacobson, P. Grundt, Org. Biomol. Chem. 11 (2013) 7455;
(e) J.N. Moorthy, K.N. Parida, J. Org. Chem. 79 (2014) 11431–11439;
(f) Y. Gao, L. Wei, Chem. Asian J. 11 (2016) 2092–2102;
(g) Q. Yu, Y. Zhang, J.-P. Wan, Green Chem. 21 (2019) 3436–3441;
(h) Y. Deng, X.-J. Wei, H. Wang, Y. Sun, T. Noel, X. Wang, Angew. Chem. Int. Ed. 56 (2017) 832–836.

[5] (a) P.P. Thottumkara, T.K. Vinod, Org. Lett. 12 (2010) 5640–5643;
(b) K.N. Parida, J.N. Moorthy, Tetrahedron 70 (2014) 2280.

[6] (a) A.M. Dumas, E. Fillion, Acc. Chem. Res. 43 (2010) 440–454;
(b) E. Fillion, A.M. Dumas, B.A. Kuropatwa, N.R. Malhotra, T.C.J. Sitler, Org. Chem 71 (2006) 409–412;
(c) A. Ashraf Wilsily, E. Fillion, Org. Lett. 10 (2008) 2801–2804;
(d) S. Ahmar, E. Fillion, Org. Lett. 16 (2010) 5748–5751;
(e) S.J. Mahoney, A.M. Dumas, E. Fillion, Org. Lett. 11 (2009) 5346–5349;
(f) M. Costa, F. Areias, L. Abrunhosa, A. Venancio, F. Proenca, J. Org. Chem. 73 (2008) 1954–1962;
(g) F. Auria-Luna, E. Marques-Lopez, M.C. Gimeno, R. Heiran, S. Mohammadi,

R.P.J. Herrera, Org. Chem 82 (2017) 5516–5523;
(h) G. Zhang, Y. Zhang, X. Jiang, W. Yan, R. Wang, Org. Lett. 13 (2011) 3806–3809;
(i) N. Fu, L. Zhang, S. Luo, Org. Lett. 17 (2015) 382–385;
(j) Z.-P. Hu, C.-L. Lou, J.-J. Wang, C.-X. Chen, M. Yan, J. Org. Chem. 76 (2011) 3797–3804;
(k) R.-J. Lu, Y.-Y. Yan, J.-J. Wang, Q.-S. Du, S.-Z. Nie, M. Yan, J. Org. Chem. 76 (2011) 6230–6239;
(l) X-G. Yin, X.-Y. Liu, Z.-P. Hu, Y. Yan, Org. Biomol. Chem. vol. 10 (2012) 1506–1509;
(m) L. Yan, H. Wang, F. Xiong, Y. Tao, Y. Wu, F. Chen, Tetrahedron: Asymmetry 28 (2017) 921–929;
(n) S. Chen, Q. Lou, Y. Ding, S. Zhang, W. Hu, J Zhao, Adv. Synth. Catal. 357 (2015) 2437–2441;
(o) N. Molleti, N.K. Rana, V.K. Singh, Org. Lett. 14 (2012) 4322–4325.
[7] T. Tsuno, K. Sugiyama, Trends Heterocycl. Chem. 7 (2001) 91.
[8] K.M. McQuaid, T.R.R. Pettus, Synlett (2004) 2403–2405.
[9] R. Caliskan, N. Nohut, O. Yılmaz, E. Sahin, M. Balci, Tetrahedron 73 (2017) 291–297.
[10] M. Suresh, A. Kumari, D. Das, R.S. Singh, J. Nat. Prod. 81 (2018) 2111–2114.
[11] (a) S.E. Denmark, D.C. Forbes, D.S. Hays, J.S. DePue, R.G. Wilde, J. Org. Chem. 60 (1996) 1391–1407;
(b) K.N. Parida, J.N. Moorthy, J. Org. Chem. 80 (2015) 8354–8360;
(c) H. Hussain, I.R. Green, I. Ahmed, Chem. Rev. 113 (2013) 3329–3371;
(d) H. Wang, H. Yang, Y. Lib, X.-H. Duan, RSC Adv. 4 (2014) 8720–8722;
(e) H. Hussain, A. Al-Harrasi, I.R. Greenc, I. Ahmedd, G. Abbas, N.U. Rehmana, RSC Adv. 4 (2014) 12882–12917;
(f) M. Zhao, J. Li, E. Mano, Z. Song, D.M. Tschaen, E.J.J. Grabowski, P.J. Reider, J. Org. Chem. 64 (1999) 2564–2566;
(g) D. Ojima, A. Yasui, K. Tohyama, K. Tokuzumi, E. Toriihara, K. Ito, A. Iwasaki, T. Tomura, M. Ojika, K. Suenaga, J. Org. Chem. 81 (2016) 9886–9894.
[12] (a) R.S. Phatake, C.V. Ramana, Tetrahedron Lett. 56 (2015) 2183–2186;
(b) R.S. Phatake, C.V. Ramana, Tetrahedron Lett. 56 (2015) 3868–3871;
(c) Y. Wang, W. Jiang, C. Huo, J. Org. Chem. 82 (2017) 10628–10634.
[13] (a) T. Tanino, S. Ichikawa, M. Shiro, A. Matsuda, J. Org. Chem. 75 (2010) 1366–1377;
(b) X.-L. Geng, Z. Wang, X.-Q. Li, C. Zhang, J. Org. Chem. 70 (2005) 9610–9613;
(c) H. Yamaoka, N. Moriya, M. Ikunaka, Org. Process Res. Dev. 8 (2004) 931–938.
[14] (a) C. Kim, T.G. Traylor, C.L. Perrin, J. Am. Chem. Soc. 120 (1998) 9513–9516;
(b) M.S. Ahmed, D.S. Mannelb, T.W. Rootb, S.S. Stahla, ACS Catal. 7 (2017) 60–69.
[15] (a) A. Kumar, V. Bhakuni, Tetrahedron Lett. 37 (1996) 4751–4754;
(b) M.J. Porter, J. Skidmore, Chem. Commun. (2000) 1215–1225.
[16] (a) L. Liu, L. Du, D. Zhang-Negrerie, Y. Du, K. Zhao, Org. Lett. 16 (2014) 5772–5775;
(b) W. Yu, Y. Du, K. Zhao, Org. Lett. 11 (2009) 2417–2420;
(c) A. Yoshimura, V.V. Zhdankin, Chem. Rev. 116 (2016) 3328–3435;
(d) Y. Zhang, H. Tan, W. Liu, RSC Adv. 7 (2017) 54017–54020.
[17] K.C. Nicolaou, V.A. Adsool, C.R.H. Hale, Org. Lett. 12 (2010) 1552–1555.
[18] H.S. Sandhu, S. Sapra, M. Gupta, K. Nepali, R. Gautam, S. Yadav, R. Kumar, S.M. Jachak, M. Chugh, M.K. Gupta, O.P. Suri, K.L. Dhar, Bioorg. Med. Chem. 18 (2010) 5626–5633.
[19] (a) L. Emmanuvel, T.M.A. Shaikh, A. Sudalai, Org. Lett. 7 (2005) 5071–5074;
(b) W. Zhong, J. Yang, X. Meng, Z. Li, J. Org. Chem. 76 (2011) 9997–10004.
[20] F. Bigi, S. Carloni, L. Ferrari, R. Maggi, A. Mazzacani, G. Sartori, Tetrahedron Lett. 42 (2001) 5203–5205.
[21] F. Bigi, M.L. Conforti, R. Maggi, A. Piccinno, G. Sartori, Green Chem. 2 (2000) 101–103.
[22] G. Cardillo, S. Fabbroni, L. Gentilucci, M. Gianotti, A. Tolomelli, Synth. Commun. 33 (2003) 1587–1594.
[23] M. Suresh, N. Kumar, G. Veeraraghavaiah, S. Hazra, R.B. Singh, J. Nat. Prod. 79 (2016) 2740–2743.
[24] D. Ngo, M. Kalala, V. Hogan, R. Manchanayakage, Tetrahedron Lett. 55 (2014) 4496–4500.
[25] L.F. Tietze, G. Brasche, A. Grube, N. Bçhnke, C. Stadler, Chem. Eur J. 13 (2007) 8543–8563.