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One-Pot Two-Step Oxidative Cleavage of 1,2-Arylalkenes to Aryl Ketones Instead of Arylaldehydes in an Aqueous Medium: A Complementary Approach to Ozonolysis[‡]

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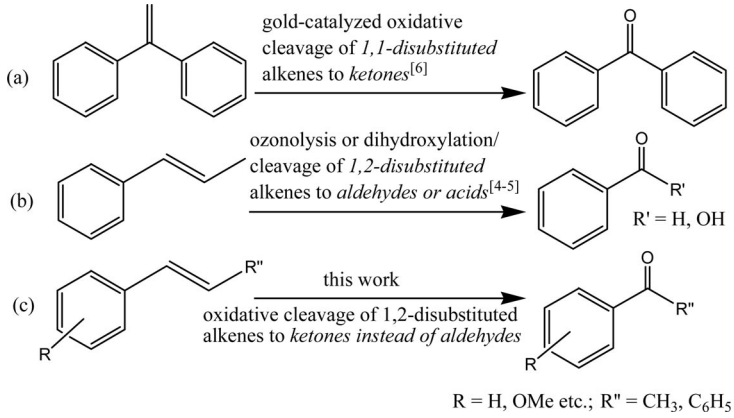
Keywords: Cleavage reactions / Alkenes / Oxidation / Ketones / Microwave chemistry

A new approach has been developed for a one-pot and selective oxidative cleavage of aryl- and 1,2-diarylalkenes leading to one-carbon shorter aryl ketones; thereby, providing a complementary approach to classical ozonolysis. The methodology was applicable to diverse aromatic and polyaromatic arylalkenes bearing electron-donating or -withdrawing groups on the aromatic ring. The protocol also provided a useful one-pot oxidative cleavage–condensation sequence, which could potentially have important applications in natural product total synthesis.

Introduction

The oxidative scission of C=C bonds is a fundamental synthetic transformation[1a–1b] and has widespread applications in organic synthesis, including the total synthesis of natural products.[1c] The major utility of such cleavage reactions is due to their ability to truncate large compounds with the simultaneous introduction of a carbonyl function. This critical transformation is usually achieved through two principal approaches, that is, ozonolysis[2] and the Lemieux–Johnson reaction[3] (dihydroxylation–cleavage sequence). In spite of their immense utility, the demanding nature of both of these strategies has spurred the exploration of improved methods. For instance, the safety concerns with ozonolysis has led to the development of some equivalent reactions with OsO_4/Oxone,[4a] trapping of carbonyl oxides,[4b] or biocatalysis.[4c] Similarly, there have been noteworthy attempts to explore the dihydroxylation–cleavage route for olefinic cleavage by using RuCl nanoparticles,[5a] $RuCl_3$/Oxone,[5b] micro-encapsulated OsO_4,[5c] H_2O_2/Na_2WO_4,[5d] and a combination of $PhI(OAc)_2$ and OsO_4 (cat.)/2,6-lutidine.[5e]



Scheme 1. Some prominent approaches for direct oxidative cleavage of 1,1- or 1,2-disubstituted arylalkenes (a, b) and the present work (c).

On the other hand, increased attention has recently been placed on developing conceptually newer olefinic cleavage approaches. For instance, the one-step C=C bond cleavage of 1,1-diaryl-substituted alkenes into ketones has been accomplished by using gold(I) complex/TBHP.[6] In another instance, $Pd(OAc)_2$ has also been employed for the oxi-

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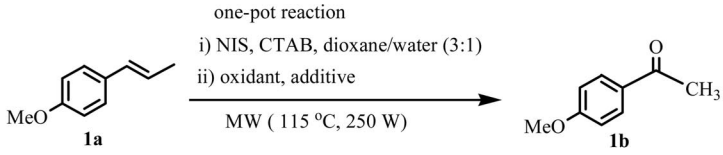
dation of alkenes by cleavage of a dioxo–Pd^{II} intermediate.[7] In spite of the utility of the above protocols, almost all of these approaches cleave 1,2-disubstituted alkenes into aldehydes, whereas ketone cleavage products are usually obtained from respective 1,1-disubstituted alkenes (Scheme 1). Thus, it is generally well recognized that the substitution pattern around an olefinic bond largely determines the nature of cleavage products. To the best of our knowledge, a general approach for the counterintutive one-step formal scission of abundantly available aryl- and 1,2-diarylalkenes into one-carbon shorter aryl ketones, instead of arylaldehydes, has not been disclosed, although in a few cases such a transformation has been noticed as a side reaction during the oxidation of stilbenes.[8]

Such a methodology would provide a useful complementary tool to the prevalent approaches[4–7] as it considerably enhances the flexibility for cleaving an olefinic bond into either aldehydes or ketones irrespective of the substitution pattern around a double bond. In this context, we herein report a one-pot oxidative cleavage approach that splits various 1,2-disubstituted arylalkenes into the corresponding aryl ketones by using *N*-iodosuccinimide (NIS) and pyridinium dichromate/*tert*-butyl hydroperoxide (PDC/TBHP) as co-oxidants with microwave (MW) heating under aqueous conditions.

Results and Discussion

In the course of our programme towards the catalytic synthesis of biologically important phenolics,[9] we initially desired to achieve a one-step conversion of abundantly available arylalkenes into the corresponding α-aryl propionic acids, which are constituents of nonsteroidal anti-inflammatory drugs (NSAIDs).[10] In this context, we planned to utilize our recently developed approach[9b] comprising direct oxidation of arylalkenes into α-arylaldehydes for an in situ oxidation[11] of such aldehydes into respective α-substituted arylalkanoic acids. Consequently, PDC was chosen as the in situ oxidizing agent due to its known ability to convert such α-substituted aldehydes into acids.[12] However, contrary to our expectations, the reaction[9b] of

Table 1. Optimization of conditions for cascade oxidative cleavage of 1,2-arylalkenes into aryl ketones under focused microwave irradiation.[a]



Entry	Oxidant	Amount of oxidant (equiv.)	Additive	Yield [b] (%)
1	PDC	6	—	41
2	PDC	3	—	64
3	PDC	1.5	—	71
4	PDC	1.2	—	61
5	PCC	1.5	—	42
6	Oxone	1.5	—	38
7	Ag_2O	1.5	—	42
8	H_5IO_6	1.5	—	29
9	TBAF	1.5	—	traces
10	CrO_3	1.5	—	23
11	$K_2Cr_2O_7$	1.5	—	62
12	TBHP	6	—	46
13	H_2O_2	6	—	41
14	PDC	1.5	CH_3COOH	79 (71)[c]
15	PDC	1.5	CF_3COOH	76
16	PDC	1.5	NaOH	61
17	PDC	1.5	L-proline	78
18	PDC	1.5	pyridine-2,5-dicarboxylic acid	76
19	PDC/H_2O_2	0.05/6	CH_3COOH	30
20	PDC/TBHP	0.05/6	CH_3COOH	35

[a] CEM monomode microwave. General conditions: **1a** (1.35 mmol), NIS (1.75 mmol), and CTAB (0.08 mmol) in dioxane (11 mL)/water (3.7 mL) were irradiated under MW conditions (115 °C, 250 W) for 15 min, followed by cooling, addition of an oxidant and, in some cases, an additive (2.0 mmol), and further MW treatment for 15 min. [b] Based on GC–MS analysis. [c] Isolated yield of pure product.

1a (C^6–C^3 unit) with NIS (1.3 equiv.) and then cetyltrimethylammonium bromide (CTAB), followed by treatment with PDC (6 equiv.)[12] in same pot under microwave conditions provided a product, the detailed GC–MS and NMR investigations of which revealed it to be one-carbon shorter acetophenone (**1b**), instead of the expected α-arylpropionic acid.[11–12] Nevertheless, the promising utility of such an approach for direct oxyfunctionalization and cleavage of even 1,2-arylalkenes into ketones instead of aldehydes[5–7] prompted us to further explore its scope and mechanistic pathway. Consequently, a detailed optimization study (Table 1) was conducted to evaluate the effect of various oxidizing agents and additives. Interestingly, the use of other well-known oxidizing agents, such as Oxone, TBHP, H_2O_2 etc., was not beneficial for oxidative cleavage of arylalkenes (Table 1, entries 6, 12–13). However, addition of a reduced amount of PDC (1.5 equiv.) led to a significantly increased yield of **1b** (71%) (Table 1, entry 3). Amongst the various acidic/basic additives, the use of acetic acid led to a further improvement in the reaction performance besides helping in the workup of the reaction mixture (Table 1, entry 14).

The apparently counterintuitive cleavage of even 1,2-disubstituted arylalkenes into aryl ketones instead of arylaldehydes implied an oxygenation–rearrangement–oxidative cleavage mechanistic pathway. Thus, arylalkene (**a**) is initially converted to the corresponding α-arylaldehyde[9b] in the presence of NIS/H_2O (**a′**). Subsequently, the oxidation of this α-arylaldehyde into an one-carbon shorter ketone can proceed through a number of intermediates,[13] including an α-aryl acid[8,13b–13c] and enol[12–13a] etc. Thus, the incipient α-arylaldehyde (**a′**) can undergo oxidation into the corresponding α-aryl acid, which is then further converted into the respective ketone through oxidative decarboxylation (Figure 1).[8,13b–13c] To evaluate the above possibility, the standard acids, that is, Flurbiprofen® [2-(2-fluorobiphenyl-4-yl)propanoic acid] or Ibuprofen® {2-[4-(2-methylpropyl)phenyl]propionic acid} were treated with PDC under identical conditions; however, the corresponding ketones were not detected. In another alternative pathway, the incipient α-arylaldehyde undergoes acid-catalyzed enolization,[12–13a] followed by PDC-assisted oxidative cleavage into the corresponding ketone (Figure 1; **b**). To further confirm the above mechanistic rationale, arylalkene (**1a**) was treated with PDC/acetic acid alone in dioxane/water (3:1) under MW conditions. Interestingly, the above reaction afforded only 4-methoxybenzaldehyde; thereby, clearly highlighting the critical role of the cascade pathway (Figure 1) in providing exclusive access to ketone cleavage products. Further, the role of the MW[14] was also evaluated by reaction of **1a** under thermal heating at a similar temperature; however, **1b** was obtained in a comparatively lower yield (55%) with longer reaction times (6 h). It is pertinent to mention here that such a cleavage of incipient α-arylaldehydes into respective one-carbon shorter ketones has earlier been observed by using reagents, such as O_2[13c–13d] (in combination with polyoxometalates/zeolite), oxidoruthenium complexes,[13e] peroxidases,[13f] and $PhI(OAc)_2$,[8] etc.

The utility of the above optimized protocol for the cleavage of C=C double bonds was subsequently ascertained. As would be evident from Table 2, various aromatic and polyaromatic arylalkenes bearing electron-donating/-withdrawing groups (EDGs/EWGs) underwent facile oxidative cleavage into the corresponding aryl ketones instead of the arylaldehydes. Further, the arylalkene with an elongated side chain (C^6–C^5 unit) was also compatible (Table 2, entry 3) with the developed methodology. On the other hand, the olefin possessing a free phenolic group (Table 2, entry 11) provided a lower yield of the respective aryl ketone owing to probable polymerization besides formation of some side products. Similarly, the relatively unactivated substrates, such as 1,1-disubstituted (Table 2, entry 14) and aliphatic alkenes (Table 2, entry 15) also led to low reaction performance, presumably due to a reduced formation of the corresponding α-substituted aldehydes in the first step (Figure 1).

To utilize the present approach for the simultaneous introduction of multiple functionalities, an one-pot halogenation–oxidative cleavage sequence was envisaged. However, the in situ reaction of **2b** (obtained from oxidative cleavage of **2a**) with NIS[15] did not afford the expected 2-iodoacetophenone (**2b′**; Scheme 2). Surprisingly, an alternative approach proved fruitful, wherein, initial treatment of **2a** with excess NIS[9b] provided the expected iodo derivative **2b′**; thereby, demonstrating the successful incorporation of both oxygen and iodo groups in a single operational step (Scheme 2).

The above success with 1,2-arylalkenes (Table 2) motivated us to explore an analogous oxidative cleavage of 1,2-diarylalkenes into the corresponding benzophenones. How-

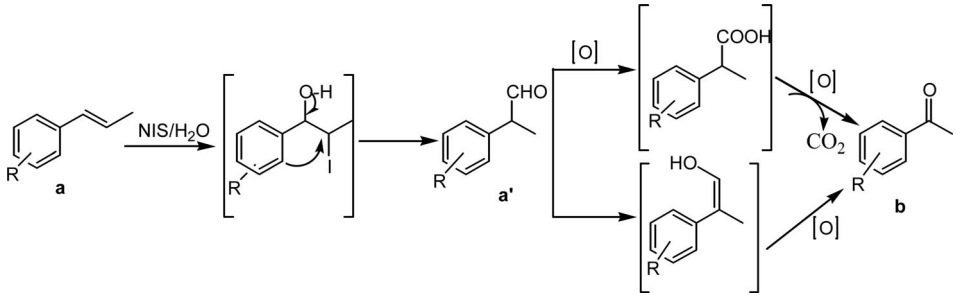
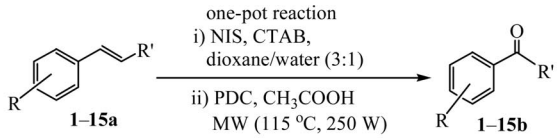
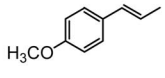
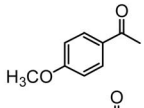
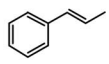
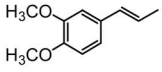
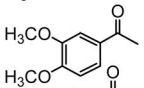
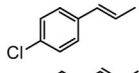
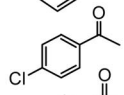
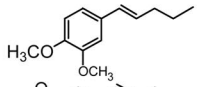
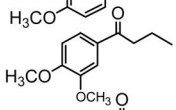
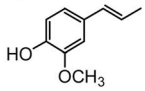
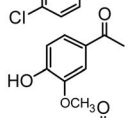
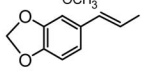
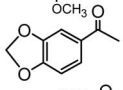
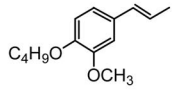
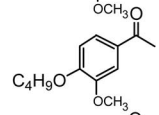
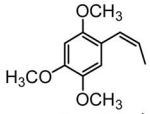
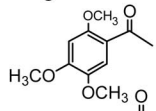
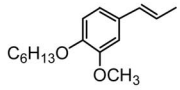
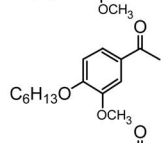
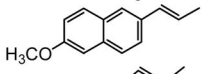
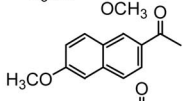
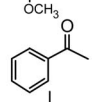
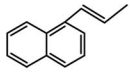
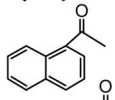
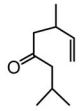
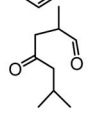
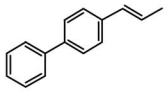
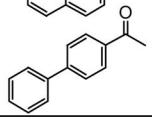


Figure 1. Plausible mechanistic pathways for one-pot oxidative cleavage of 1,2-disubstituted arylalkenes into one-carbon shorter ketones.

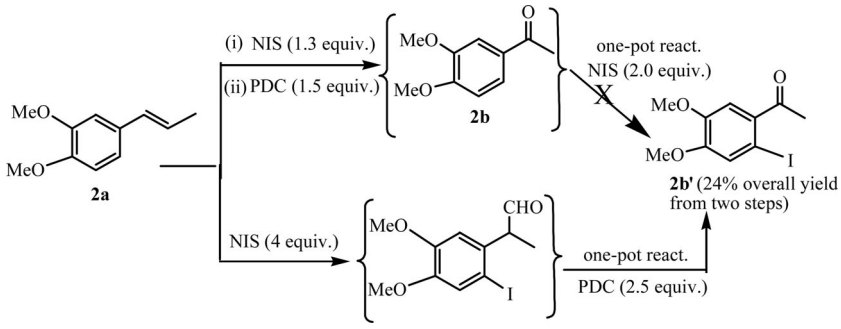
Table 2. Cascade oxidative cleavage of 1,2-arylalkenes into aryl ketones instead of benzaldehydes under focussed microwave irradiation.[a]



R = H, OMe, OH, OCH_2O, Cl, C_6H_5, OC_4H_9, OC_6H_{13} etc.
R' = CH_3, $CH_2CH_2CH_3$ etc.

Entry	Substrate (a)	Product (b)	Yield[b] (%)	Entry	Substrate (a)	Product (b)	Yield[b] (%)
1			71	9			37
2			78	10			30[c]
3			51	11			14[c]
4			86	12			76
5			45[c]	13			48
6			67	14			12[c]
7			54	15			n.d.[c–d]
8			23				

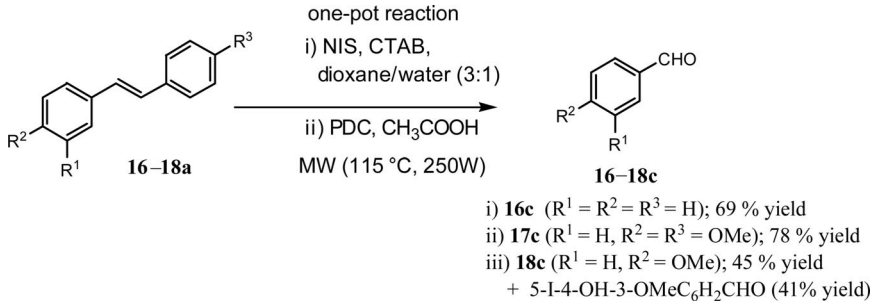
[a] CEM monomode microwave. General conditions: substrate (0.9 mmol), NIS (1.18 mmol), and CTAB (0.08 mmol) in dioxane (11 mL)/water (3.7 mL) were irradiated under MW conditions (115 °C, 250 W) for 15 min, followed by cooling and addition of PDC (1.36 mmol) and CH_3COOH (1.36 mmol) and further MW treatment for 15 min. [b] Yield of pure isolated product (single run). The structure of all products was confirmed by NMR spectroscopy (^1H and ^{13}C) and HRMS analysis. [c] Based on GC–MS. [d] Not detected.



Scheme 2. One-pot halogenation–oxidative cleavage of an arylalkene.

ever, the developed protocol did not provide the expected result, even as parent stilbenes were selectively cleaved into benzaldehydes (Scheme 3).

In view of above result and the well-known tendency of such diarylalkenes towards cleavage into benzaldehydes,[5c] a reduced amount of PDC (0.8 equiv.) was also tried but to

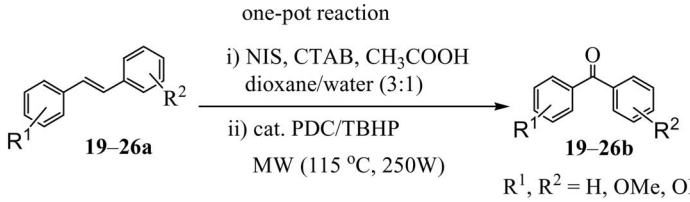


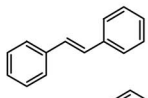
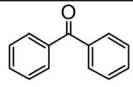
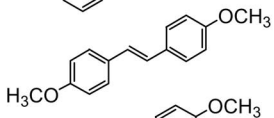
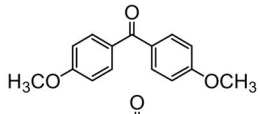
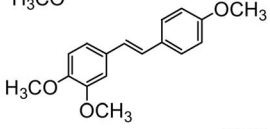
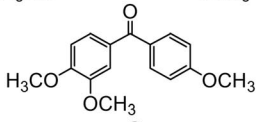
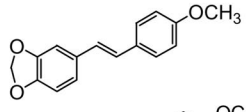
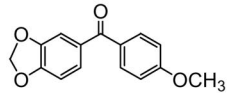
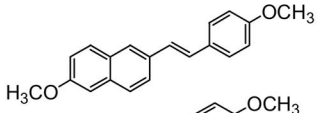
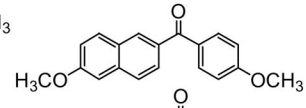
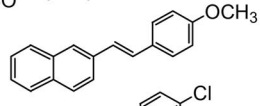
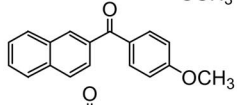
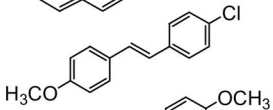
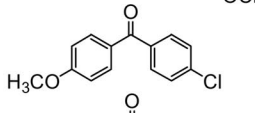
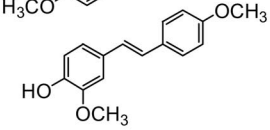
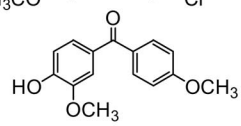
Scheme 3. Selective oxidative cleavage of symmetrical and unsymmetrical 1,2-diarylalkenes into benzaldehydes.

no avail. On the other hand, the use of other oxidizing agents, such as H_2O_2, TBHP, and $K_2Cr_2O_7$ etc., did provide the desired benzophenone **19b** but in low yields.

Further, some unreacted starting 1,2-diarylalkene was also obtained by using the above reaction conditions. Thereafter, detailed studies were conducted for identifying

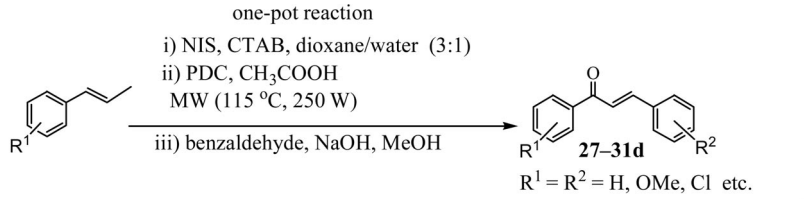
Table 3. Cascade oxidative cleavage of 1,2-diarylalkenes into benzophenones instead of benzaldehydes under focused microwave irradiation.[a]

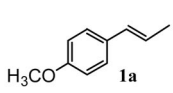
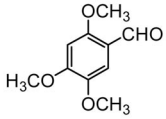
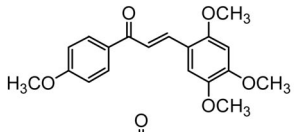
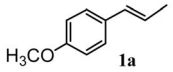
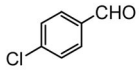
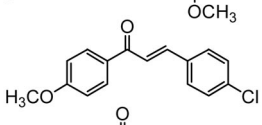
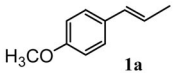
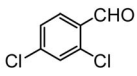
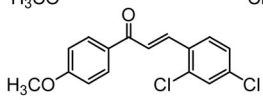
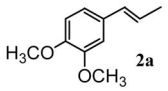
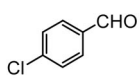
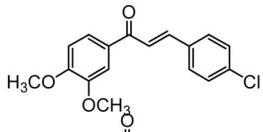
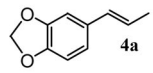
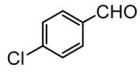
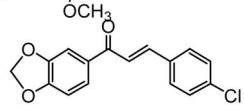


Entry	Substrate (a)	Product (b)	Yield[b] (%)
19			49
20			60
21			63
22			67
23			29
24			31
25			65
26			15[c]

[a] CEM monomode microwave. General conditions: substrate (0.79 mmol), NIS (1.5 mmol), CH_3COOH (1.16 mmol), and CTAB (0.08 mmol) in dioxane (11 mL)/water (3.7 mL) were irradiated under MW conditions (115 °C, 250 W) for 15 min, followed by cooling and addition of PDC (0.04 mmol)/TBHP (4.7 mmol) and further MW treatment for 15 min. [b] Yield of the pure isolated product (single run). The structure of all products was confirmed by NMR spectroscopy (^1H and ^{13}C) and HRMS analysis. [c] Based on GC–MS.

Table 4. One-pot oxidative cleavage–condensation of alkenes with benzaldehydes under focused microwave irradiation.[a]



Entry	Alkene (a)	Benzaldehyde	Product (d)	Yield[b] (%)
27				56
28				60
29				34
30				52
31				68

[a] CEM monomode microwave. General conditions: alkene (1.35 mmol), NIS (1.75 mmol), and CTAB (0.08 mmol) in dioxane (11 mL)/water (3.7 mL) were irridated under MW conditions (250 W, 115 °C) for 15 min, followed by cooling and addition of PDC (2.0 mmol). CH_3COOH (2.0 mmol) was then added and MW treatment was continued for 15 min. Thereafter, 10% NaOH (5–8 mL) and a methanolic solution (2–3 mL) of benzaldehyde (1.48 mmol) was added and the resulting mixture was stirred for 2 h. [b] Overall yield of pure isolated product from arylalkene (single run).

an oxidation system compatible with such 1,2-diarylalkenes. Interestingly, a combination of catalytic PDC (0.05 equiv.) along with TBHP (6 equiv.) as a co-oxidant was optimum to afford the desired **19b** (Table 3, entry 19) in an enhanced 49% yield. In addition, the use of acetic acid along with an increased amount of NIS [2 equiv. in place of 1.3 equiv. (Table 2)] at the start was required to overcome the initial sluggish conversion of such diaryl-substituted alkenes into the corresponding iodohydrins (Figure 1). Subsequently, the above reaction conditions were also found to be applicable to various unsubstituted, electron-rich and -deficient 1,2-diarylalkenes with aromatic or polyaromatic cores (Table 3). It is pertinent to mention that the oxidative cleavage of olefins into benzophenones has been earlier reported by using only 1,1-diaryl-substituted C=C double bonds.[5b,6,7] In this context, the developed methodology affords the first direct scission of even 1,2-disubstituted olefins into the corresponding benzophenones.

After having developed a new approach for the oxidative cleavage of diverse arylalkenes, we were intrigued to evaluate further applications of this methodology. In this context, we were attracted by several reports of the total synthesis of natural products, wherein a two-step sequence of oxidative cleavage followed by condensation[16] has comprised an important strategy. Consequently, the realization of an one-pot protocol for tandem oxidative cleavage–condensation would be beneficial as it would eliminate the isolation of intermediates.[16] As a proof of concept, **1a** was subjected to the developed oxidation protocol (Table 2) till formation of **1b** occured, and, thereafter, a base, such as NaOH (10%) and 2,4,5-trimethoxybenzaldehyde (1.3 equiv.), was added to the same pot and stirred for 2 h. Gratifyingly, this one-pot approach proved useful to directly obtain the condensation product **27d** from the corresponding arylalkenes in a 56% overall yield (Table 4, entry 27). Later on, the above one-pot strategy was also successfully applied to various other arylalkenes (Table 4); thereby, providing a hitherto unknown route to the one-step oxidation–condensation of olefinic bonds.

Conclusions

We have developed a new oxidative cleavage approach that affords for the first time a selective scission of 1,2-disubstitued alkenes into one-carbon shorter ketones by using NIS and PDC/TBHP as co-oxidants. As the classical approaches like ozonolysis predominantly involve cleavage of 1,2-disubstituted alkenes into aldehydes, the developed methodology considerably enhances the flexibility for cleav-

ing an 1,2-disubstituted olefinic bond into either ketones or aldehydes. Moreover, the reaction showed a wide substrate scope as diverse 1,2-aryl and diarylalkenes bearing electron-donating or -withdrawing groups underwent facile cleavage into the corresponding aryl ketones. Significantly, the protocol also paved the way for a valuable one-pot oxidative cleavage–condensation reaction, which has widespread utility in the total synthesis of natural products. Further investigations to improve the scope of the developed reaction are currently underway.

Experimental Section

General: β-Asarone was obtained from natural *Acorus calamus* oil by following our earlier reported procedure.[17a] The naphthyl and stilbene derivatives were prepared through a previously reported Grignard–dehydration[9c] or Heck approach,[17b] respectively. All of the above synthesized alkenes were fully characterized by ^{1}H and ^{13}C NMR spectroscopy before further use. The rest of the arylalkenes were reagent grade (purchased from Merck and Aldrich). NIS was reagent grade (Merck) and used as such without any further purification. Glacial acetic acid (99–100% for synthesis) and PDC (pyridinium dichromate) and other oxidants were used as supplied. The solvents used for isolation/purification of compounds were obtained from commercial sources and used without further purification. Column chromatography was performed by using silica gel (60–120 mesh size). ^{1}H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Bruker Avance-300 spectrometer. HRMS-ESI spectra were determined by using a micromass Q-TOF ultima spectrometer. GC–MS analysis was carried out on Shimadzu MS-QP-2010 system equipped with a Stationary phase DB-5MS column (Agilent Technologies, U.S.A.). A CEM Discover focused microwave (2450 MHz, 300 W) was used wherever mentioned. The temperature of reactions in microwave heating experiments was measured by an inbuilt IR temperature probe that determined the temperature on the surface of reaction flask. The sensor is attached in a feedback loop with an on-board microprocessor to control the temperature rise rate. For the case of conventional heating in an oil bath, the temperature of the reaction mixture was monitored by an inner thermometer.

Representative Procedure for the One-Pot Oxidative Cleavage of Arylalkenes into One-Carbon Shorter Aryl Ketones: Water (3.7 mL), CTAB (0.03 g, 0.08 mmol), and NIS (0.26 g, 1.18 mmol) were added to a stirred mixture of 4-butoxy-3-(methoxyphenyl)propene (Table 2, entry 12, 0.2 g, 0.9 mmol) and dioxane (11 mL) and the mixture was allowed to stir for 5 min at room temperature. Subsequently, the flask was irradiated under a focused microwave system (250 W, 115 °C) for 15 min. Thereafter, the above reaction flask was cooled and acetic acid (0.08 mL, 1.36 mmol) and PDC (0.51 g, 1.36 mmol) were added and the mixture further irradiated under microwave conditions (250 W, 115 °C) for 15 min. The above mixture was cooled, washed with saturated aq. $Na_2S_2O_3$ solution (1 × 10 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine (1 × 10 mL), dried with Na_2SO_4, and vacuum evaporated. The obtained residue was subsequently purified by column chromatography on silica gel (60–120 mesh size) by using hexane/ethyl acetate (9.3:0.7) to give 4′-butoxy-3′-methoxyacetophenone (**12b**) (0.152 g, 76% yield) as a cream-coloured solid.

4′-Butoxy-3′-methoxyacetophenone (12b): See Table 2. Cream-coloured solid. IR (KBr): $\tilde{\nu}$ = 1674 (C=O) cm^{-1}, m.p. 35–37 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (t, J = 6.5 Hz, 2 H, Ar), 7.08 (s, 1 H, Ar), 4.30 (t, J = 7.1 Hz, 2 H), 4.07 (s, 3 H), 2.78 (s, 3 H), 2.12–2.04 (m, 2 H), 1.79–1.67 (m, 2 H), 1.23 (t, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 197.0, 153.1, 149.4, 130.4, 123.4, 111.2, 110.6, 68.9, 56.2, 31.1, 26.3, 19.3, 14.0 ppm. HRMS-ESI: calcd. for $C_{13}H_{18}O_3$ [M + H]$^+$ 223.1302; found 223.1302.

The above procedure was also used for the oxidative cleavage of all the other arylalkenes (Table 2, entries 1–11, 13–15). The structures of the corresponding products were confirmed by NMR spectroscopy (^{1}H and ^{13}C), HRMS, or GC–MS analysis (see Supporting Information).

Representative Procedure for the Cascade Oxidative Cleavage of 1,2-Diarylalkenes into Benzophenones: Water (3.7 mL), CTAB (0.03 g, 0.08 mmol), NIS (0. 35 g, 1.5 mmol), and acetic acid (0.07 mL, 1.16 mmol) were added to a stirred mixture of *trans*-4′-methoxy-3,4-(methylenedioxy)stilbene (Table 3, entry 22; 0.2 g, 0.79 mmol) and dioxane (11 mL) and the reaction mixture was allowed to stir for 3–4 h at room temperature. Subsequently, the flask was irradiated under MW conditions (250 W, 115 °C) for 15 min. Thereafter, the reaction flask was cooled, PDC (0.015 g, 0.04 mmol) and TBHP (0.45mL, 4.7 mmol) were added and the mixture was further irradiated under microwave conditions (250 W, 115 °C) for 15 min. The above mixture was cooled, washed with saturated aq. $Na_2S_2O_3$ solution (1 × 10 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine (1 × 10 mL), dried with Na_2SO_4, and vacuum evaporated. The obtained residue was subsequently purified by column chromatography on silica gel (60–120 mesh size) by using hexane/ethyl acetate (9.3:0.7) to give 4′-methoxy-3,4-(methylenedioxy)benzophenone (**22b**) (0.13 g, 67% yield) as a white solid.

4′-Methoxy-3,4-(methylenedioxy)benzophenone (22b): See Table 3. White solid, m.p. 96–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, J = 9.7 Hz, 2 H, Ar), 7.33 (d, J = 9.3 Hz, 2 H, Ar), 7.00 (d, J = 9.7 Hz, 2 H, Ar), 6.95 (d, J = 8.0 Hz, 1 H, Ar), 6.07 (s, 2 H, OCH_2O), 3.89 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 194.4, 163.3, 151.5, 148.2, 132.9, 132.6, 131.0, 126.6, 113.9, 110.3, 108.0, 102.1, 55.9 ppm. HRMS-ESI: calcd. for $C_{15}H_{12}O_4$ [M + H]$^+$ 257.0808; found 257.0806.

The above procedure was also used for the oxidative cleavage of all the other 1,2-diarylalkenes (Table 3, entries 19–21, 23–26). The structures of the corresponding products were confirmed by NMR spectroscopy (^{1}H and ^{13}C) and HRMS analysis (see Supporting Information).

Representative Procedure for the One-Pot Oxidative Cleavage–Condensation of Arylalkenes with Benzaldehydes: Water (3.7 mL), CTAB (0.03 g, 0.08 mmol), and NIS (0.395 g, 1.75 mmol) were added to a stirred mixture of 4-(methoxyphenyl)propene (Table 4, entry 27; 0.2 g, 1.35 mmol) and dioxane (11 mL), and the reaction mixture was allowed to stir for 5 min at room temperature. Subsequently, the flask was irradiated under MW conditions (250 W, 115 °C) for 15 min. The mixture was then cooled and acetic acid (0.12 mL, 1.99 mmol) and PDC (2.0 mmol) were added and MW treatment (250 W, 115 °C) was continued for 15 min. Thereafter, the reaction mixture was filtered and 5–8 mL of 10% sodium hydroxide (till basic conditions) along with a methanolic solution (2–3 mL) of 2,4,5-trimethoxybenzaldehyde (0.29 g, 1.48 mmol) were added. The reaction mixture was allowed to stir for 2 h, after which, it was washed with saturated aq. $Na_2S_2O_3$ solution (1 × 10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine (1 × 10 mL), dried with Na_2SO_4, and vacuum evaporated to give a crude mixture which upon addition of methanol led to the precipitation of condensation

product 1-(4′-methoxyphenyl)-3-(2,4,5-trimethoxyphenyl)-2-propen-1-one (**27d**) (0.24 g, 56% yield) as a light-yellow solid.

1-(4′-Methoxyphenyl)-3-(2,4,5-trimethoxyphenyl)-2-propen-1-one (27d): See Table 4. Light-yellow solid, m.p. 107–110°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10–8.00 (m, 3 H, Ar, C*H*), 7.50 (d, J = 16.6 Hz, 1 H, C*H*), 7.12 (s, 1 H, Ar), 6.96 (d, J = 8.0 Hz, 1 H, Ar), 6.50 (s, 1 H, Ar), 3.87 (s, 3 H, OCH_3), 3.85 (s, 6 H, OCH_3), 3.84 (3 H, S, OCH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 189.6, 163.5, 154.9, 151.8, 143.1, 139.6, 132.0, 130.8, 120.5, 116.5, 114.1, 112.0, 97.1, 57.3, 57.0, 56.3, 56.2 ppm. HRMS-ESI: calcd. for $C_{19}H_{20}O_5$ $[M + H]^+$ 329.1383; found 329.1387.

The above procedure was also used for the one-pot oxidative cleavage–condensation of all the other arylalkenes (Table 4, entries 28–31). The structures of the corresponding products were confirmed by NMR spectroscopy (^{1}H and ^{13}C) and HRMS analysis (see Supporting Information).

Supporting Information (see also the footnote on the first page of this article): Complete experimental details and spectroscopic data of compounds.

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